THE JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR

Volume X, No. 1

January-February, 1955

IN ENGLISH TRANSLATION

CONSULTANTS BUREAU
152 West 42nd St., New York 18, N.Y.

—An agency for the interpretation of international knowledge—

The Journal of Analytical Chemistry of the U.S.S.R. in English Translation

January-February, 1955

TABLE OF CONTENTS

	Page	Russ. page
1. Refractometric Analysis of Ternary Systems. B. V. Joffe and A. G. Morachevsky	1	3
2. X-Ray Spectrographic Determination of Hafnium in Zirconium Minerals and Concentrates. E. E. Vaimshtein, I. D. Shevalevsky and I. F. Shtauberg	11	14
3. Quantitative Spectrographic Analysis of Hafnium in Zirconium. G. Kryuger, R. R. Shvangiradze and T. A. Mozgovaya	15	20
4. Colorimetric Determination of Vanadium by Means of a Catalytic Reaction. V. A. Nazarenko and E. A. Biryuk	21	28
5. Organic Coprecipitants. 2. Coprecipitation of Tungsten with Organic Coprecipitants. V. I. Kuznetsov, M. N. Chozhin and E. S. Palshin	25	32
6. Potentiometric Titration Using the Catalytic Decomposition of Hydrogen Peroxide on a Platinum Electrode. I. E. Flis	31	38
7. Potentiometric Determination of $Cr_2O_7^{2-}$ Ions and Strong Acids when Both Are Present Simultaneously. I. E. Flis and Zh. L. Veri	37	44
8. Functional Analytical Groups for Iron and Bismuth. N. M. Turkevich	41	47
9. Micro Determination of Carbon in Metals. P. A. Kryukov and E. V. Rengarten	45	51
10. Precipitation of Quadrivalent Vanadium with 5,7-Dibromo- and 5,7-Diiodo-8-hydroxyquinoline. I. P. Alimarin and V. G. Kryukov	49	56
11. Diphenylcarbazone as a Reagent for the Colorimetric Determination of Germanium. G. S. Desmuk	53	61
12. A Specific Reaction for Formaldehyde. G. Vanag and E. Vanag	55	63
13. Characteristic Chromatographic Reactions for Glucose and Acetone. F. M. Shemyakin and O. S. Lobakhina	57	65
Criticism		
14. R. Přibil, "Complexones in Chemical Analysis", Czech. Acad. Sci. Press, Prague, 1953, pp. 167, Price 24 Crowns (Kcs.). Reviewed by R. P. Lastovsky	61	69
Chronicle		
15. The Conference on the Application of Complex Compounds in Analytical Chemistry held from October 25-27, 1954 at Ivanovo	63	71

THE JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR

Volume X, No. 1

January-February, 1955

Editor

A. P. Vinogradov

Editorial Board

I. P. Alimarin, A.M.Dymov, E.S.Przhevalsky, D.I.Ryabchikov (Secretary), Z. F. Shakhova, I. V. Tananaev (Deputy Editor)

Collaborators

A.K.Babko, S. A. Borovik, M. L. Chepelevetsky, Yu.A.Chernikhov, A.A. Grinberg, P. A. Kashinsky, A.S.Komarovsky, M.A.Konstantinova-Schlezinger, I.M.Korenman, S.E.Krasikov, Yu. Yu. Lurye, Yu. V. Morachevsky, K.A.Nenadkevich, V.I.Petrashen, N.K.Pshenitsyn, A. K. Rusanov, S.A. Strelkov, N. A. Tananaev, A. N. Terenin, A. M. Vasilyev, N. I. Vlodavets, S.I.Volfkovich

(A Publication of the Academy of Sciences of the USSR)

IN ENGLISH TRANSLATION

Copyright, 1955

CONSULTANTS BUREAU

152 West 42nd Street

New York 36, N.Y.

Printed in the United States

Annual subscription $80.00
Single issue 20.00

Note: The sale of photostatic copies of any portion of this copyright translation is expressly prohibited by the copyright owners. A complete copy of any paper in this issue may be purchased from the publisher for $7.50.

BLANK
PAGE

REFRACTOMETRIC ANALYSIS OF TERNARY SYSTEMS

B. V. offe and A. G. Morachevsky

The A. A. Zhdanov Leningrad State University

In order to carry out a complete analysis of a ternary system it is necessary to determine two independent parameters characterizing its composition, in particular, any two physical properties. Usually, density and refractive index are used for this purpose. To ensure the necessary experimental accuracy for density determinations of $1\text{-}2\cdot10^{-4}$ g/ml, a few milliliters of test mixture is required, i.e., 10-20 times more than is required for refractive index determination (0.05-0.5 ml). In many cases, however, this necessity of using minimum amounts of test material is an essential factor, and limits the possibility of using methods involving density determinations.

The rapidity and ease with which refractive index measurements can be made with a high degree of accuracy, and with minimal expenditure of test mixture makes it very desirable to work out analytical methods for ternary systems which are based only on refractive index measurements.

No special study has been made of the possibility of analyzing ternary mixtures on the basis of refractometric results alone, and there are only isolated cases of the application of such methods. Thus, it was proposed recently [1], to analyze the systems water–acetone–n-butyl alcohol, and water–acetone–dioxane by determining the refractive index n_D at two temperatures (20 and 40°). The method is applicable to systems whose components differ sufficiently both in their n_D and in the temperature coefficient $\frac{\Delta n_D}{\Delta t}$. The analytical errors of such determinations in the systems indicated amount to 1-2% for measurements of n_D with an accuracy of up to $2\cdot10^{-5}$ (precision refractometer).

Another example is the group analysis of gasoline fractions arbitrarily considered as ternary mixtures of aromatic, naphthenic, and paraffinic hydrocarbons [2]. This method consists in determining n_D^{20} of a test sample before and after removal of aromatic hydrocarbons by sulfonation.

An original technique of refractometric analysis was used recently for the system benzene–butylbromide–nitrobenzene [3]. Determination of the composition was carried out by measuring n_D of a test sample, and n_D of the mixture of the test sample with an accurately weighed aliquot of one of the components, or with a mixture of these components of known concentration. Calculations were carried out graphically on the basis of a triangular diagram constructed beforehand with a net work of iso-refractive lines, and a supplementary graph drawn for each test sample. This method involves a considerable expenditure of time and a fairly large amount of test mixture (for taking an accurate aliquot); the advantages of refractometric methods are, therefore, not made use of.

This article deals with two fairly widely used refractometric methods of analyzing ternary systems. The first is based on measurements of refractive dispersion, and the second on extraction of one of the components with a suitable reagent or solvent.

The Dispersometric Method

If the components of a ternary system differ appreciably from each other not only with respect to refractive index but also with respect to refractive dispersion, then in order to determine the composition of a three component mixture, in principle, it is sufficient to measure two refractive indices at different wavelengths λ_1 and λ_2. A study of experimental results on the dispersion of organic compounds permits them to be divided into two main groups:

I. Compounds with high dispersion (relative dispersion $\omega_{FCD} > 27$) aromatic compounds and heterocyclic compounds with an "aromatic character", (a number of thiophenes, pyridines, pyrroles, etc.) with not very complex aliphatic radicals; aliphatic and alicyclic compounds containing systems of two or more conjugated double or ternary bonds; iodo-derivatives of all classes; the simplest metallo-organic compounds of lead, mercury, cadmium and zinc.

II. Compounds with low dispersion. ($\omega_{FCD} < 22$) compounds not containing short carbon-carbon bonds (paraffinic and cycloparaffinic hydrocarbons, alcohols, ketones, aldehydes, acids, ethers and esters, amines, amides, nitriles, chloro derivatives, and mono-bromo derivatives) and also the majority of compounds with one short carbon-carbon bond. Water belongs to this class ($\omega_{FCD} = 17.9$).

Analysis of ternary systems by means of n_{λ_1} and n_{λ_2} (for dispersion measurements with an accuracy of 0.1-0.2%) can be realized in practice if two of the components are from one of the groups indicated above, and differ sufficiently in their refractive indices, while the third component belongs to the other of the two groups given above.

In general, dispersometric analysis requires a preliminary study of the relations between n_{λ_1} and n_{λ_2} and the concentration of the ternary mixtures, and construction of a triangular diagram with iso-refraction lines for n_{λ_1} and n_{λ_2} (or better n_{λ_1} and $n_{\lambda_2}-n_{\lambda_1}$). The diagram obtained can be used directly for graphical determination of the composition of the test ternary mixture from the values of n_{λ_1} and n_{λ_2}. Nevertheless, if the components of the system do not include materials which dissociate strongly, or react chemically with one another, (normal, in particular hydrocarbon systems) then dispersometric analysis can be carried out by the method described below without any difficult preliminary study of ternary mixtures of known composition, and the construction of triangular diagrams.

We shall use the following notation: n, n_1, n_2 and n_3 for the refractive indices of the mixture and its components (for the same temperature and wavelength); Δ, Δ_1, Δ_2 and Δ_3 the respective dispersions of the mixture and its components for wavelengths λ_1 and λ_2: $\Delta = n_{\lambda_1} - n_{\lambda_2}$, λ_1 and λ_2 should not be too close, for the rest the choice of wavelengths can be determined by considerations of convenience; V_1, V_2 and V_3 the concentrations of the components in fractions of unity, by volume.

It is known [4], that the shape of $n(V)$ curves approximate to a straight line in normal systems. Calculations show that small deviations of $n(V)$ from additivity in normal binary systems usually approximate to corrected terms of the type $k_{ij}V_iV_j$, where k_{ij} is a constant for all mixtures of components i and j.

Assuming that the constants k maintain their values even in ternary mixtures, it is possible to write:

$$n = n_1V_1 + n_2V_2 + n_3V_3 + k_{n_{12}}V_1V_2 + k_{n_{13}}V_1V_3 + k_{n_{23}}V_2V_3. \quad (1)$$

Then, for a particular dispersion we have a similar relation:

$$\Delta = \Delta_1V_1 + \Delta_2V_2 + \Delta_3V_3 + k_{\Delta_{12}}V_1V_2 + k_{\Delta_{13}}V_1V_3 + k_{\Delta_{23}}V_2V_3 \quad (2)$$

($k_{\Delta_{12}}$, $k_{\Delta_{13}}$ and $k_{\Delta_{23}}$ are the constants of the deviation of a particular dispersion from additivity).

Remembering that

$$V_1 + V_2 + V_3 = 1, \quad (3)$$

it is possible to find V_1, V_2 and V_3 (i.e., to determine the composition of the ternary mixture) by solving the system of equations (1), (2) and (3).

The simplest method of carrying out such calculations is that of successive approximation. First, the concentrations of the components are calculated to the first approximation, ignoring the deviations of n and Δ from additivity:

$$V'_1 = \frac{(\Delta-\Delta_3)(n_2-n_3)-(n-n_3)(\Delta_2-\Delta_3)}{(n_2-n_3)(\Delta_1-\Delta_3)-(n_1-n_3)(\Delta_2-\Delta_3)}, \quad (4)$$

$$V'_2 = \frac{(n-n_3)(\Delta_1-\Delta_3)-(\Delta-\Delta_3)(n_1-n_3)}{(n_2-n_3)(\Delta_1-\Delta_3)-(n_1-n_3)(\Delta_2-\Delta_3)}. \quad (5)$$

V'_3 is determined by subtracting the sum of V'_1 and V'_2 from unity. The approximate value of V' is then used for calculating the corrections for deviations from additivity, a and b:

and

$$a = k_{n_{12}}V_1V_2 + k_{n_{13}}V_1V_3 + k_{n_{23}}V_2V_3, \quad (6)$$

$$b = k_{\Delta_{12}}V_1V_2 + k_{\Delta_{13}}V_1V_3 + k_{\Delta_{23}}V_2V_3. \quad (7)$$

The concentrations of the components are then calculated to the second (final) approximation (V''_1, V''_2 and V''_3), by substituting $n-a$ instead of n and $\Delta-b$ instead of Δ in equations (4) and (5).

TABLE 1

The Original Results for Dispersometric Analysis of Ternary Hydrocarbon Mixtures (numeration of the components corresponds to the order of their enumeration in the systems)

Constants		The system toluene–methylcyclohexane–n-heptane	The system secondary butyl benzene–secondary butylcyclohexane–di-isoamyl
Refractive index n_C^{20}	n_1	1.4922	1.4864
	n_2	1.4210	1.4443
	n_3	1.3859	1.4064
Mean dispersions Δ_{FC}^{20}	Δ_1	159.9	137.5
	Δ_2	75.2	78.2
	Δ_3	66.9	71.7
Constants of the deviations of the refractive index from additivity	$k_{n_{12}}$	−0.0080	−0.0037
	$k_{n_{13}}$	−0.0045	−0.0024
	$k_{n_{23}}$	−0.0005	0
Constants of the deviations of the mean dispersion from additivity	$k_{\Delta_{12}}$	−4.0	−2.9
	$k_{\Delta_{13}}$	−4.0	−2.4
	$k_{\Delta_{23}}$	±0.0	0

Thus, this variant of the dispersometric method which is suggested for systems with small deviations of $\underline{n}$ and Δ from additivity only requires a knowledge of the constants $\underline{k}_n$ and k_Δ corresponding to binary systems and measurements of the two indices $\underline{n}_{\lambda_1}$ and $\underline{n}_{\lambda_2}$ of the test mixture.

The suitability of the proposed method for determining the components of ternary mixtures of aromatic hydrocarbons with naphthenes and paraffins, was checked by analyzing synthetic mixtures of the system toluene–methylcyclohexane–heptane and of the system secondary butyl benzene–secondary butyl cyclohexane–di-isoamyl.

The compounds used for making up the synthetic mixtures were the same preparations as those used by one of us previously for the study of binary hydrocarbon systems [5]. 7-15 g of the mixtures were prepared by weight. Refractive indices were determined on a Pulfrich refractometer for the two hydrogen lines F and C. They were measured with an accuracy of up to $1 \cdot 10^{-4}$ for n_C^{20} and $2\text{-}3 \cdot 10^{-5}$ for the difference $n_F^{20} - n_C^{20}$.

Original results for calculation of the analytical values by means of equations (4-7) are adduced in Table 1. Refractometric results published previously [5], for the corresponding binary systems were used for calculating the constants $\underline{k}_n$ and k_Δ.

Table 2 contains results on the measurements of n_C^{20} and $\Delta_{FC}^{20} = (n_F^{20} - n_C^{20}) \cdot 10^4$ for ternary mixtures, and results of the determination of the composition of these mixtures by the method described. The results obtained show that the dispersometric method proposed, in conjunction with careful use of the Pulfrich refractometer permits determination of the composition of ternary systems of the type aromatic hydrocarbon–naphthene–paraffin, with an error of less than 1%.

The Extraction Method

If one of the components can be quantitatively removed by a suitable reagent or solvent in which the remaining components are practically insoluble, then in many cases it is more expedient to determine the composition of ternary systems by measurement of the refractive index before and after extraction of one of the components.

In order to check on the possibility of using such a method, and to get some idea of a suitable solvent to use, one can take as a guide the classification of organic compounds according to their solubility as used in qualitative organic analysis [6].

Solvents which are very widely used are concentrated aqueous solutions of sulfuric and phosphoric acids (for the extraction of many oxygen and nitrogen containing low molecular weight organic compounds) and concentrated alkali solutions (for removal of compounds of an acid character, carboxylic acids, sulfonic acids, phenols, etc.).

The possibility of carrying out quantitative extraction by means of the chosen solvent must be checked experimentally in each individual case.

Particularly favorable conditions for applying the extraction method are obtained in cases of systems where one of the components is an oxygen- or nitrogen-containing organic compound, and where the two other components are inert compounds of the "I" class (paraffins, cycloparaffins, aromatics, and halogen derivatives). 75-80% sulfuric acid is a good selective solvent for the analysis of mixtures of this type.

As we showed experimentally, by shaking with a ten-fold volume of 80% sulfuric acid the following representatives of various classes or organic compounds can be practically completely removed from their mixtures with benzene;

TABLE 2

Results of the Analysis of Ternary Hydrocarbon Mixtures by a Dispersometric Method

n_C^{20}	Δ_{FC}^{20}	Content of aromatic hydrocarbon as a fraction of the total volume				Content of naphthenic hydrocarbon as a fraction of total volume			
		added	found		error	added	found		error
		v_1	v'_1	v''_1	$v''_1 - v_1$	v_2	v'_2	v''_2	$v''_2 - v_2$
The System toluene–methylcyclohexane–heptane									
1.4331	103.2	0.3830	0.3704	0.3787	−0.0043	0.2283	0.2229	0.2372	+0.0089
1.4226	81.3	0.0899	0.0843	0.0866	−0.0033	0.7978	0.7902	0.8003	+0.0025
1.4184	84.7	0.1565	0.1419	0.1532	+0.0033	0.4815	0.4745	0.4873	+0.0058
The System secondary butylbenzene–secondary butyl cyclohexane–di-isoamyl									
1.4497	97.3	0.3557	0.3489	0.3581	+0.0024	0.4070	0.4058	0.4049	−0.0021
1.4436	91.9	0.2681	0.2654	0.2731	+0.0050	0.4245	0.4214	0.4211	−0.0034
1.4250	75.0	0.0000	0.0021	0.0021	+0.0021	0.4784	0.4863	0.4863	+0.0079

methyl-, ethyl-, n- and isopropyl-, and isobutyl alcohols, dioxane, methyl ethyl ketone, diacetyl alcohol, acetonyl acetone, mesityl oxide, acetic acid, diethyl acetamide, diethyl nitrosamine, aniline and butylidenebutylamine.*

In addition to the completeness and selectiveness of the extraction, another necessary condition for accurate analysis is that there is sufficient difference between the refractive indices of the components. For measurements of n up to $1 \cdot 10^{-4}$ accurately to a tenth of a percent, analysis by the extraction method is possible for the following approximate ratios:

1) the difference in the refractive indices of the non-extracted components exceeds 0.01-0.02;

2) the refractive index of the extracted component should differ by not less than 0.01 from the refractive index of the non-extracted component with the greater refractive index, and from that of the non-extracted component with the lower refractive index.

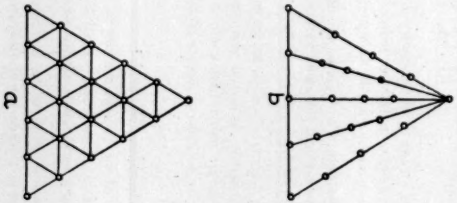


Fig. 1. Methods of preparing ternary mixtures for studying the relation between refractive index and composition.

If these approximate conditions are not fulfilled, it does not always exclude the possibility of using the extraction method, but it does mean that the accuracy is lowered, or the application of the method is confined to a limited concentration range.

* Experiments were carried out with a 67% (vol) solution of the compounds indicated in benzene; n for the residue after shaking for 1-2 minutes differed from n for the original benzene by not more than $2 \cdot 10^{-4}$.

Analysis by the method described requires establishment of the relation between refractive index and the concentrations of the components of the ternary systems beforehand. To do this, n must be determined for the corresponding binary systems and for several series of ternary systems arranged regularly on a triangular diagram of composition by one of two methods:

1) on lines of constant concentration for one of the components as shown in Fig. 1, a;

2) on intersections with a constant ratio for the concentrations of two of the components (Fig. 1, b). The first method of preparing the mixtures is more difficult (since it requires taking aliquots of the components, calculated beforehand) but nevertheless permits the path of the isotherm for n to be discerned more clearly for a minimum number of mixtures. In the second method, ternary mixtures are prepared from the binary mixtures and the third component; in this case there is no need to make preliminary accurate calculations and the aliquots can be varied within certain limits.

An auxiliary graph of n-composition is constructed for each of the test lines and the values of n interpolated at various intervals (e.g., at intervals of 0.0001). The interpolated values are plotted on a triangular diagram of large size and points of equal n joined by smooth curves. As a result a graph is obtained which can be used directly for determining the composition of test ternary mixtures. Such a diagram is shown in Fig. 2 for the system benzene-cyclohexane-isopropyl alcohol; the method of using the diagram is also indicated.

A search is made among the iso-refractive lines (i.e., lines which join points in the system with equal refractive indices) for lines which correspond respectively to the measured refractive index of the test mixture ($n_{mixture}$), and to the value of the refractive index of the residue (a binary mixture) after removal of one of the components.

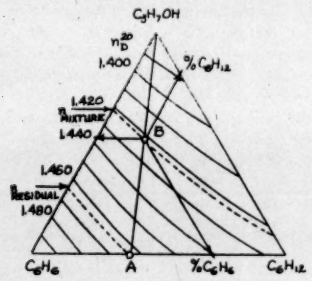


Fig. 2. Diagram used for the analysis of ternary mixtures by the extraction method.

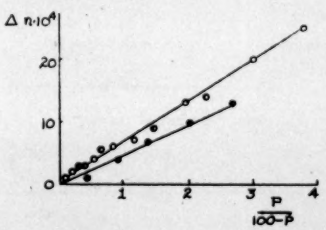


Fig. 3. Relation between deviation Δn between $n_{orig.}$ for the mixture of benzene and cyclohexane and $n_{residual}$ after removal of isobutyl alcohol from the ternary mixture, and the alcohol content. ◐ = the line intersecting the ratio benzene : cyclohexane = 27.3:72.7; O = the same for the ratio 52.1:47.9; ● = a ratio 77.6:22.4.

These iso-refractive lines are shown in Fig. 2 by dotted lines. The point of intersection of the iso-refractive line for $n_{residual}$ with the side joining the apices representing the two non-extracted components (i.e., the line joining C_6H_6 to C_6H_{12}) (Point A), is joined by a straight line to the opposite apex of the triangle (C_3H_7OH). This straight line, which represents a constant ratio of the concentration of benzene to that of cyclohexane, intersects the iso-refractive line $n_{mixture}$ at the point B, the coordinates of which represent the percentage composition of the test mixture. The extraction method was worked out in detail and checked on systems of the type benzene–cyclohexane–alcohol, the alcohols being n-propyl, isopropyl and isobutyl alcohols in turn.

Alcohol is removed by 75% sulfuric acid (~ 3 ml) by vigorous shaking for 1-2 minutes in a small test tube (5 ml capacity) fitted with a ground glass stopper.* 0.2 ml of a test mixture is sufficient for a determination if the alcohol content is not too high. After settling, the top (hydrocarbon) layer is accurately removed with a pipet and transferred to the refractometer prism. n_D^{20} measurements are made on an Abbe refractometer so that all the analysis takes only a few minutes. The suitability of this method of removing alcohols was demonstrated in preliminary experiments in which it was established that a) the refractive index of a binary mixture of benzene–cyclohexane does not change at all under such a treatment;

b) the alcohol can be completely removed from ternary mixtures, while if the alcohol content is not high (up to 20-30%) then n_D^{20} of the remaining hydrocarbon layer differs from n_D^{20} of the original binary mixture of benzene and cyclohexane by not more than 0.0002 (on the low side).

* It is best to use a specially constructed small separating funnel.

** By the original mixture we mean the binary mixture of benzene and cyclohexane, by addition of alcohol to which the standard ternary mixtures are obtained.

TABLE 3

Refractive Indices of Binary Mixtures of Benzene, Cyclohexane, and Iso-propyl Alcohol

Benzene–Cyclohexane		Benzene–Isopropyl Alcohol		Cyclohexane–Isopropyl Alcohol	
% mol alcohol	n_D^{20}	% mol alcohol	n_D^{20}	% mol alcohol	n_D^{20}
0.00	1.4263	0.00	1.5011	0.00	1.4263
17.19	1.4355	9.05	1.4901	10.66	1.4210
20.00	1.4369	13.08	1.4852	17.04	1.4181
27.52	1.4415	17.35	1.4802	20.00	1.4168
34.56	1.4459	20.00	1.4770	28.34	1.4130
40.00	1.4493	26.00	1.4699	32.03	1.4113
45.87	1.4534	29.78	1.4655	37.14	1.4090
52.01	1.4579	33.88	1.4608	40.40	1.4077
60.00	1.4640	38.98	1.4548	41.56	1.4070
64.37	1.4675	40.00	1.4536	46.04	1.4060
70.39	1.4726	50.00	1.4412	50.00	1.4029
80.00	1.4811	60.00	1.4291	60.00	1.3983
100.00	1.5011	80.00	1.4040	80.00	1.3882
		100.0	1.3773	100.00	1.3773

Increasing the alcohol concentration leads to an increase in the deviations Δn, which at very high alcohol concentrations (greater than 60-70%) increases very rapidly and may affect the third place of decimals by several units.

The results in Fig. 3 show that the deviations between $n_{residual}$ and $n_{original}$ for the binary mixture of benzene and cyclohexane which are observed on extracting the alcohol with acid are proportional to the ratio of the alcohol content of the ternary mixture (P%), and to the hydrocarbon content (100–P). This phenomenon can be easily explained if one remembers that the solution of alcohol in sulfuric acid formed on extraction of the alcohol with acid, dissolves the hydrocarbon to an appreciable extent (as compared with pure 80% acid). By assuming that the solubility of the hydrocarbon in the acid layer is proportional to the concentration of alcohol in the acid layer, and that this is different for benzene and cyclohexane, it is possible to show that small changes in the concentration of the hydrocarbon layer (and consequently of the deviation Δn) will be proportional to the ratio $\frac{P}{100-P}$, irrespective of the ratio of the volumes of acid and test mixture, as observed experimentally (Fig. 3).

TABLE 4

Refractive Indices of Ternary Mixtures of Benzene, Cyclohexane, and Iso-propyl Alcohol

Content in mol.-%			n_D^{20}
Benzene	Cyclohexane	Iso-propyl alcohol	
20.0	20.0	60.0	1.4123
20.0	40.0	40.0	1.4202
40.0	20.0	40.0	1.4352
60.0	20.0	20.0	1.4581
40.0	40.0	20.0	1.4219
20.0	60.0	20.0	1.4283

TABLE 5

Results of the Analysis of Ternary Mixtures of Benzene, Cyclohexane, and Iso-propyl Alcohol by the Extraction Method

Actual content in mol. %			% Mol. found by analysis			Absolute error in %		
benzene	cyclo-hexane	alcohol	benzene	cyclo-hexane	alcohol	benzene	cyclo-hexane	alcohol
20.5	21.4	58.1	20.4	21.8	57.8	−0.1	+0.4	−0.3
38.0	23.3	38.7	37.9	23.6	38.5	−0.1	+0.3	−0.2
61.9	22.4	15.7	61.9	22.5	15.6	0.0	+0.1	−0.1
39.4	42.5	18.1	39.3	42.8	17.9	−0.1	+0.3	−0.2
18.0	60.4	21.6	17.9	60.8	21.3	−0.1	+0.4	−0.3

The solubility of the "non-extracted" components in the acid layer leads to inaccurate analyses in ternary mixtures whose composition corresponds to points in the diagram near the apex of the extracted component, but does not affect the accuracy of analysis of mixtures whose composition corresponds to points in the lower and middle parts of the diagram (Fig. 2). If required, the accuracy of the analysis of mixtures containing high percentages of alcohol may be increased by introducing corrections to $n_{residual}$ by means of a graph similar to Fig. 3, which can be easily constructed from the results of analysis of known mixtures used for constructing the triangular diagram.

Tables 3 and 4 contain the original results for analyses of the system benzene–cyclohexane–isopropyl alcohol by the recommended method. Table 4 contains the minimum number of results necessary for constructing the diagram used for calculating. In actual fact a considerably greater number of ternary mixtures were studied.

Table 5 contains results obtained while checking the method for ternary mixtures of benzene, cyclohexane and isopropyl alcohol. As the results from this table show the experimental error amounts to 0.2% on an average, and does not exceed 0.4%. The systematic nature of the error (0.1-0.2% low for the benzene and alcohol content and

TABLE 6

Refractive Indices of Binary and Ternary Mixtures of Isobutyl Alcohol with Cyclohexane and Benzene

Hydrocarbon Components	% weight alcohol	n_D^{20}	Hydrocarbon Components	% weight alcohol	n_D^{20}
Cyclohexane	0.00	1.4263	Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4593	53.76	1.4239
Cyclohexane	20.24	1.4188	Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4593	65.92	1.4162
Cyclohexane	35.72	1.4140	Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4593	79.14	1.4085
Cyclohexane	52.01	1.4094	Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4626	29.38	1.4450
Cyclohexane	75.57	1.4026	Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4626	61.13	1.4205
Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4423	22.51	1.4306	Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4626	83.41	1.4066
Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4423	37.67	1.4236	Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4802	29.68	1.4526
Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4423	48.98	1.4184	Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4802	47.31	1.4378
Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4423	69.06	1.4096	Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4802	57.93	1.4291
Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4522	23.10	1.4379	Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4802	72.76	1.4172
Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4522	54.88	1.4204	Benzene	0.00	1.5011
Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4522	76.96	1.4085	Benzene	25.17	1.4709
Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4593	18.75	1.4462	Benzene	51.41	1.4428
Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4593	32.82	1.4370	Benzene	76.85	1.4176
Mixture of $C_6H_6 + C_6H_{12}$ with n_D^{20} 1.4593	44.11	1.4294	–	100.0	1.3960

0.3% high for cyclohexane) is apparently connected with the appreciable solubility of benzene in the sulfuric acid layer as noted above.

Exactly similar results were obtained for the system benzene–cyclohexane–n-propyl alcohol.

Table 6 contains the original results for the analysis of benzene–cyclohexane–isobutyl alcohol mixtures. In contrast to the other systems mentioned above, the triangular diagram for this system was constructed according to scheme b (Fig. 1).

TABLE 7

Results of Analyses of Ternary Mixtures of Benzene, Cyclohexane, and Isobutyl alcohol by the Extraction Method

Actual content, in weight %			Content found by analysis, in wt. %			Absolute error, in %		
benzene	cyclo-hexane	alcohol	benzene	cyclo-hexane	alcohol	benzene	cyclo-hexane	alcohol
47.9	44.1	8.0	47.7	44.1	8.2	−0.2	±0.0	+0.2
0.0	76.0	24.0	0.0	75.7	24.3	±0.0	−0.3	+0.3
38.2	35.1	26.7	38.2	35.6	26.2	±0.0	+0.5	−0.5
0.0	52.6	47.4	0.0	52.2	47.8	±0.0	−0.4	+0.4
11.3	29.5	59.2	10.8	30.5	58.7	−0.5	+1.0	−0.5
			11.0•	29.7•	59.3•	−0.3•	+0.2•	+0.1•
13.0	11.9	75.1	12.5	13.0	74.5	−0.5	+1.1	−0.6
			12.9•	12.2•	74.9•	−0.1•	+0.3•	−0.2•
25.8	7.5	66.7	25.3	7.8	66.9	−0.5	+0.3	+0.2
			25.3•	7.6•	67.1•	−0.5•	+0.1•	+0.4•

• Corrections introduced for the solubility of the hydrocarbons in the acid layer according to Fig. 3.

Analytical results for the control mixtures (Table 7) show that for alcohol contents up to 50% (by weight), the mean accuracy is +0.2% and not more than 0.5%. In mixtures with high alcohol concentrations (up to 75%) errors of up to 1-1.1% are observed, which can, however, be eliminated by introducing the corrections mentioned for the solubility of the hydrocarbons using Fig. 3.

In conclusion, we should like to point out that the amount of preparatory work involved in constructing the diagrams for calculation can be considerably shortened if the mixtures to be analyzed fall within a limited concentration range. In the simplest case, where it is only necessary to determine the composition of one mixture (e.g., a ternary azeotrope), construction of a triangular diagram is, in general, unnecessary, since it is sufficient to determine the position of the intersect (by means of $n_{residual}$) on which the test mixture is located, prepare 2-4 synthetic ternary mixtures with the same ratio of non-extracted components, construct a graph of n-composition for this intersect, and determine the concentration of the test mixture by means of it.

SUMMARY

1. The analysis of ternary systems on the basis of refractive index measurements alone has been considered, and conditions for carrying out such an analysis by two methods worked out, the two methods are: dispersometric –by measurements of the refractive index for different wavelengths– and an "extraction method", which consists in determining the refractive index before, and after, removal of one of the components by means of a suitable reagent or solvent.

2. For normal mixtures, with small deviations of the refractive index from additivity, the proposed variant of the dispersometric method does not require preliminary study of the ternary mixtures. By control analysis of ternary mixtures of an aromatic hydrocarbon with a naphthenic and paraffinic hydrocarbon it has been shown that the proposed method permits determination of the composition of a system of this type with an error of less than 1%.

3. The extraction method is applicable to the analysis of systems of the type: aromatic hydrocarbon–saturated hydrocarbon–aliphatic alcohol. Experimental verification has demonstrated the possibility of determining the composition of the ternary mixture of benzene and cyclohexane with n-propyl, isopropyl, and isobutyl alcohols, respectively, with an accuracy of up to 0.2%.

4. The suggested analytical methods for ternary systems require only refractometric results and are characterized by the ease and speed with which they can be carried out with a minimal amount of test mixture (0.2-0.5 ml).

Received June 19, 1954

LITERATURE CITED

[1] W. M. Spicer, L. H. Meyer, Anal. Chem., 23, 663 (1951).

[2] H. M. Love, A. R. Padgett, W. D. Seyfried, H. M. Singleton, Anal. Chem., 19, 37 (1947).

[3] R. Ginell, A. Silverman, J. Am. Chem. Soc., 73, 1596 (1951).

[4] B. V. Ioffe, J. Gen. Chem., 23, 190 (1953).*

[5] B. V. Ioffe, J. Appl. Chem., 26, 397 (1953),**; J. Anal. Chem., 5, 290 (1950).

[6] R. Schrainer and R. Fuson, "Systematic Qualitative Analysis of Organic Compounds", Chapter VI, Foreign Lit. Press (1950).

---

* See Consultants Bureau Translation, page 195.

** See Consultants Bureau Translation, page 359.

BLANK
PAGE

X-RAY SPECTROGRAPHIC DETERMINATION OF HAFNIUM IN ZIRCONIUM MINERALS AND CONCENTRATES

E. E. Vainshtein, I. D. Shevaleevsky and I. F. Shtauberg

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Acad. Sci., USSR, Moscow

Despite the fact that the discovery of hafnium is one of the outstanding achievements made with the aid of the X-ray spectrographic method, the quantitative determination of this element in the presence of zirconium, which always accompanies it in the natural state, is one of the most difficult problems which confronts the X-ray spectroscopist in practice. This is the result of the fact that in trying to solve this problem one comes up against something which rarely happens in X-ray spectroscopy, viz., the practically complete superposition (at some orders of reflection) of one of the most intense lines of the accompanying elements on the most important analytical lines of the test element. The high excitation potential of the lines of the K-series of hafnium means that only the lines of the L-series can be used for analysis. The brightest of these is the α_1 line, this is followed by β_1, β_2, α_2 and λ_1. In the first order reflection the wavelengths $L\alpha_1$ (λ = 1566.33 XE) and $L\alpha_2$ (λ = 1577.19 XE) of the hafnium lines only differs by 2.27 XE and 0.17 XE respectively, from the wavelengths $K\alpha_1$ (λ = 784.30 XE) and $K\alpha_2$ (λ = 788.51 XE) of the zirconium lines in the second order reflection [1]. As for the other lines of hafnium, in decreasing order of intensity, the $L\beta_2$ line, e.g., coincides with the $L\beta_1$ line of tantalum which could be used as a reference element for hafnium analysis. This was one of the reasons which induced Hevesy and Coster [2], who were the first to use X-ray spectrographic analysis for studying the distribution of hafnium in zirconium minerals, to refrain from using tantalum which was first used as a reference standard, and to replace it by lutecium. The lines $HfL\beta_1$ (λ = 1371.25) and $LuL\beta_2$ (λ = 1367.26) were chosen as the analytical pair. Analysis was carried out using the method of "equalized blackenings". For this purpose the ratios between the atomic contents of these elements were established empirically, for which the intensities of the analytical lines chosen were equal; synthetic mixtures of the oxides of hafnium, zirconium, and lutecium were used. It was shown, however, that this occurs when one atom of hafnium corresponds to 2.6 atoms of lutecium.

Another analytical procedure was proposed by Borovsky and Blokhin [3], who were the first in the Soviet Union to make systematic studies of the hafnium content of zirconium raw materials. Because lutecium is not readily available, and is expensive, they did not use it for their mineral analysis Tantalum, which was added to the test sample as the pentoxide, was used as the reference element. Analysis was carried out by comparing the intensities of the $L\beta_1$ line of hafnium and the $TaL\beta_1$ and $HfL\beta_2$ lines which coincide with each other. To exclude interference from $HfL\beta_1$, which is superimposed on the $L\beta_1$ line of tantalum, the authors used the known ratio between the intensities of the $L\beta_1$- and $L\beta_\Gamma$- lines of the test element. This enabled them to calculate the intensity of the $L\beta_\Gamma$ line of hafnium on the basis of experimental results on the intensities of the $L\beta_1$ line of the element and to introduce the necessary corrections. For a relatively high hafnium content in the test sample (> 1%), these authors carried out their analysis by means of the $L\gamma_1$ lines of both elements, viz., the lines $HfL\gamma_1$ (λ = 1176.56 XE) and $TaL\gamma_1$ (λ = 1135.64 XE), which are free from superposition. When this was done, as calculation showed, and as was verified experimentally, under identical photographic conditions, the intensity of the $L\gamma_\Gamma$ line of hafnium is approximately 6% more intense than the equivalent line of tantalum.

Thus, in all the methods used hitherto for the quantitative determination of hafnium in minerals, analysis has been carried out on the basis of the weak $L\beta_\Gamma$ and $L\gamma_\Gamma$ lines of this element. This inevitably leads to lower sensitivity and accuracy. It seemed to us expedient, therefore, to develop some other method for determining small amounts of hafnium in zirconium minerals, in which it would be possible to make use of the strongest lines in the X-ray spectrum of this element. For this purpose it should be possible to take advantage of the fact that the analytical lines of hafnium and the superimposed upon them zirconium lines, have different excitation potentials. For hafnium, the potential is 11.3 Kv, while for zirconium it is 18 Kv. If, therefore, in mineral analysis one selects an operating voltage on the X-ray tube of the spectrograph which is near to, or equal to, the excitation potential of the zirconium line, then it should be possible, irrespective of the percentage of this element in the test, to prevent the appearance of its lines on the spectrogram, or at least weaken them appreciably. This should free the most intense hafnium line from masking by the superimposed zirconium line (at high voltage) and prevent results from being distorted. In addition,

operating the tube at a low voltage, and passing a relatively small current through it permits one to reckon on a decrease in anode heating and an increase in the stability of the test material during analysis. This should have a favorable effect on the accuracy of quantitative determinations. True, this same factor, viz., the small excess voltage for the hafnium line which at best (at U = 18 Kv) amounts to only 60% of the excitation potential of the line, puts a limit to the sensitivity of the method* and makes the intensity of the line dependent to a greater extent than in other cases, on variations in the operating voltage applied to the X-ray tube of the apparatus. Therefore, in developing an analytical technique, it is essential to take special steps to decrease the absorption of the rays during their passage from the X-ray tube anode to the photographic plate, and to maintain the excitation conditions of the spectra constant.

The present investigation was carried out on a vacuum X-ray tube spectrograph operating "on reflection" (see Fig. 1, (see plate page 65)). The apparatus was a spectrograph of the Johann type issued by the Experimental Mechanical Factory of the USSR Academy of Sciences Petroleum Institute, which we modified in our laboratory. Practically all the most important parts of the apparatus were changed. The construction of the X-ray tube was modified, as well as the system of fixing the anode to the body of the apparatus, the vacuum system was overhauled and the set-up arranged in such a way that the vacuum in the body of the instrument and in the X-ray tube could be directly controlled. The system of fixing the photographic plate in the spectrograph cell was improved and a new mechanism for rocking the cell introduced, the anode was oil-cooled, and a number of other auxiliary instruments prepared, which facilitated operation of the instrument, and permitted standardization of many of the stages of the operations. These modifications permit the apparatus to be used to its best advantage and lead to more rapid and accurate analysis. The set-up of the X-ray tube is schematically shown in Fig. 2. The test sample is placed on one of the faces of a tetrahedral anode 1 which is arranged relative to the cathode 2, in such a way that the electron beam focused by the cylinder 3, after emission by the oxidized filament of the cathode, forms a focal spot on the center of one of the faces of the anti-cathode. The anode is fixed to the spectrograph body 4 by means of a bush 5, and once it has been centered it may be freely rotated around its axis and fixed in position by means of a clamping screw (not shown in Fig. 2). The outside of the bush holding the anode has four marks on it so that it is possible to determine the rotation angle of the anode, thus bringing into operation any of the four faces of the tetrahedral anode. This rotation can be accomplished in the evacuated apparatus without breaking the vacuum. The body of the X-ray tube 6, as usual, is a turned cylindrical detail with an internal diameter of ~30 mm; it has a tubule 7, through which the X-rays are passed. Rubber is used for packing the vacuum, 8. This type of set-up enables one to analyze four samples in a row without dismantling any of the apparatus (the four samples are placed on the faces of the anode), to accomplish this it is only necessary to ensure that the film in the spectrograph is shifted on when the anode is rotated, and to prevent any stray radiation getting onto the spectrogram. This was achieved as follows (Fig. 3). A flexible steel band, 1, is fitted in the focal plane of the cell; this band is fitted with a small right angled slit through which the X-rays can pass to fix the lines of the test and reference elements respectively on the X-ray film. The X-ray film is firmly pressed against the outer side of the cell at the place where the slit is by means of a special rubber roller, 2, which is fitted with a clamp made of a polished steel band. When the film is being turned in the focal plane of the apparatus, the roller can rotate freely about its axis. The pressure which it exerts on the film depends on the resilience of the spring, 4. A simple gadget shown in Fig. 3 is used for pulling the film past the slit. The basis of this is a steel lever, 5, fastened by a hinge to the body of the spectrograph cell. The short arm of lever 5 connects with the head of screw 7, fastened to the central bush of the spectrograph, via a vertically arranged strip, 6. The bush is also connected by the system of levers, 8, to the cell, 9. This enables the cell to be arranged in the required position by moving the lever securely fixed to the bush and fitted on the outside of the apparatus. In order to move the film relative to the cell slit, the end of the film is fastened in a special clamp, 10, fitted at one end of the arms of the lever, 5. When lever 5 is fixed in the position shown in Fig. 3 and the cell is rotated through a certain angle in counter-clockwise direction, the film will be pulled along the incident and focal places through a distance which depends on the angle of rotation of the cell

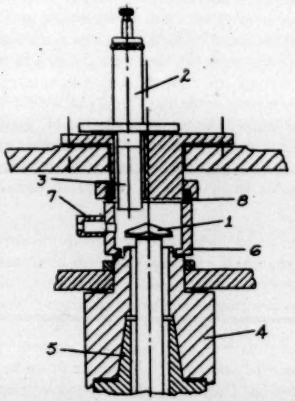


Fig. 2. The X-ray tube of the spectrograph.

* It restricts the value of the maximum intensity of the $L\alpha_1$ line of hafnium.

and the ratio of the arms of lever 5. When the film has been advanced in the cell through a distance which can be established once and for all for the cell, then by rotating the cell in the opposite direction it can be fixed in the operating position, in which the X-rays reflected from the crystal corresponding to the chosen lines of the test element can fall on the slit in the focal plane of the spectrograph. It is obvious that for an uninterrupted and regular forward movement of the film in a succession of tests, the angle of the first rotation of the cell in the counter-clockwise direction should increase all the time like the series of an arithmetical progression. The type of tube and set-up described proved to be very convenient to use in practice. They enable analyses to be speeded up considerably.

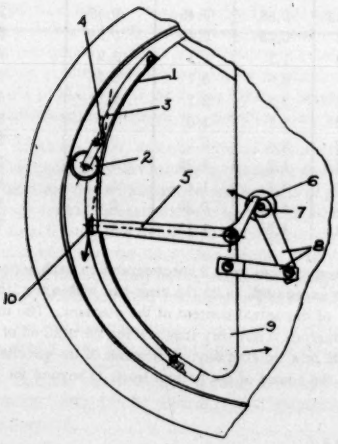


Fig. 3. Film moving mechanism of the spectrograph.

A quartz lamina cut along the surface of a rhombohedron (in the $10\bar{1}1$ face) was used as the refleeting crystal of the spectrograph. The lattice constant was $\underline{d}$ = 3,33 A. Using this crystal the linear dispersion of the spectrograph in the part of the spectrum we were interested in was ~11,5 XE/mm. Quantitative determination of hafnium was made by means of the $L\alpha_1$ line of the element in the second order of reflection. The $L\alpha_1$ lines of tantalum or lutecium were used as reference lines. In order to cut down the intensity of the $K\alpha_1$ line of zirconium, which for the first order reflection is located at a distance of only ~5 XE from the analytical line for hafnium, experiments were carried out at a voltage of 18 Kv. Under these conditions, the zirconium line is either completely absent (U < 18 Kv) or its intensity becomes so small that its presence does not interfere with the photometric measurements of the line of the test element. It was shown in a series of tests that for the photographic material chosen, and the development conditions used, spectrograms with greatest contrast are obtained for a current of 12-15 mA and a 10 minute exposure. For shorter exposure times, the line intensity is insufficient for reliable photometric measurements. In order to increase the contrast of the photographs, and decrease the background on the spectrograms, an attempt was made to use an anti-cathode made of a lighter material – aluminum – instead of the conventional copper. The reduction in background on the spectrograms obtained in this way was shown to be ~10-15%. On the other hand, however, heating of the sample during analysis was considerably greater than when copper anti-cathodes were used, so that there was no point in switching over to aluminum anti-cathodes. The spectra were recorded on "Agfa" film or on uni-layer aero film. The films were developed at 18-20° in a specially constructed thermostat in which the temperature was kept constant to within 0,5°. Development time was selected experimentally. It varied from 6 to 12 minutes for various films; 40 ml of fresh developer was used for a film approximately 18 X 190 mm in area. The reference element was added to test sample as the oxide. Under the chosen experimental conditions, blackening of the lines on the spectrograms did not exceed 0,7-0.8. When carrying out large numbers of determinations of the element in raw materials, and in products containing the element during processing, the method of interpolation by standards was also widely used. A group of zircons which had been carefully analyzed for hafnium and a number of synthetic mixtures containing 0,05; 0,1; 0,3; 0,7; 1,0; 3,0; 5,0; 7,0 and 10% of the reference elements were used as the standards. Spectrograms of the test and reference elements were taken on the same plate. For the analysis of hafnium in samples by the method of interpolation by standards, the blackening of the line of the test element was compared with the blackening of the equivalent line of the reference element in standards containing an amount of element near to that being determined. The hafnium concentration range, from 0,1 to 10%, was divided into two (0,1-1% and 1-10%); within these two ranges the conditions employed differed slightly, so that the proportionality between blackening and line intensity was not lost. It was shown experimentally that in each of these concentration ranges there is a linear relation between the difference of blackenings of the lines and background, and the content of the element in the sample. On this basis, when comparing lines with similar blackenings, calculation of the content of the element in the sample was made by means of linear interpolation. The MF-2 photometer was used for photometric measurements of the spectrograms,

as well as a simplified model of the MF-2 made in our laboratory and shown in Fig. 4 (see plate, page 65). The stability of test material with exposure time on the anticathode of the X-ray tube, in the absence, within the limits of experimental accuracy, of a systematic change in analytical results was checked experimentally; this was also checked by comparing the analytical results of a series of determinations carried out one after the other without renewing the amount of material on the anode faces. Reproducibility was determined in a special series of tests and was found to be of the order of 5%. Three independent series of experiments (I, II, III) were carried out in order to check on the accuracy of the method. The results of these tests are adduced in the Table. Each of the figures adduced

Sample No.	Hafnium content I	II	III	Mean	Error %	Sample No.	Hafnium content I	II	III	Mean	Error %
1	0.6	0.7	0.6	0.6	5.5	12	0.65	0.55	0.45	0.55	12.0
2	1.3	1.2	1.1	1.2	5.5	13	0.5	0.55	0.45	0.5	6.5
3	1.1	1.0	1.0	1.0	3.0	14	1.3	1.2	1.1	1.2	5.5
4	1.2	1.4	1.0	1.2	11.0	15	—	0.8	0.7	0.75	6.5
5	1.0	1.0	1.0	1.0	0	16	2.3	2.3	2.1	2.3	3.0
6	1.3	1.5	0.95	1.25	16.0	17	1.0	1.1	1.0	1.0	3.0
7	1.2	1.1	1.0	1.1	6.0	18	2.3	2.4	2.0	2.3	6.0
8	3.0	2.8	1.8	2.6	18.0	19	1.25	1.2	1.25	1.25	1.5
9	0.3	0.4	0.4	0.4	8.0	20	1.0	1.1	1.1	1.1	3.0
10	0.4	0.4	0.4	0.4	0	21	0.9	0.95	0.95	0.95	1.5
11	1.2	1.2	1.2	1.2	0	22	1.15	1.20	1.15	1.15	1.5

in the first three columns is the mean of three independent determinations from 9 spectrograms in each series of experiments. In 15 of the 22 results adduced the error does not exceed 6%, in 20 the error lies within the limits of 12% and only in two cases is the error 16 and 18% respectively, of the actual content of the element. The mean arithmetical error is 5.6%. The time required to carry out an analysis is not very long. When the method of interpolation by standards is used, 10-15 determinations can be made in a working day. Discussion of the geochemical conclusions to be drawn from the analytical results obtained in the course of the present work, is beyond the scope of this article.

SUMMARY

1. An X-ray spectrographic method is described for the determination of hafnium in zirconium minerals and concentrates, in which the most intense line of the L-series can be used for the quantitative determination of the element. Analysis is carried out by means of a vacuum X-ray spectrograph working on "reflection". In order to prevent interference from zirconium the operating voltage applied to the X-ray tube is maintained at a level near to the excitation potential of the line for the K-series of this element.

2. It has been shown that quantitative determination of hafnium by the method described is possible starting at contents of 0.2-0.3%. Reproducibility and the mean arithmetic experimental error is approximately 5%.

Received August 25, 1954

LITERATURE CITED

[1] E. Vainshtein and M. Kakhana, "Tables of X-ray Spectroscopic Lines", Acad. Sci. Press, Moscow, 1953.

[2] G. Hevesy, "X-ray Chemical Analysis and its Applications", State Sci. Tech. Press., Moscow-Leningrad, 1940.

[3] I. Borovsky and M. Blokhin, Bull. Acad. Sci., Phys. Series I, 185 (1937).

QUANTITATIVE SPECTROGRAPHIC ANALYSIS OF HAFNIUM IN ZIRCONIUM

G. Krynger, R. R. Shvangiradze, and T. A. Mozgovaya

Introduction

Determination of small amounts of hafnium in zirconium entails a number of difficulties. The earlier analytical method that was used for analysis of mixtures of hafnium and zirconium was determination of the atomic weight of these mixtures [1, 2], this method; however, is inapplicable at low concentrations of one of the components. X-ray spectrographic analysis permits determination of hafnium in zirconium in amounts of 0.5% upward [3]. Radiochemical methods, which are based on measurements of the cross section of neutron capture or determination of the intensity of radiation of the active hafnium isotope obtained by neutron irradiation, require powerful neutron sources [4]; radiochemical methods are, therefore, only applicable in special cases.

In recent years, determination of hafnium in zirconium – particularly determination of traces of hafnium – has been carried out predominantly by means of emission spectrographic analysis [5-8]. Among the papers devoted to this question, that of Mortimore and Noble is of particular interest. They succeeded in achieving a high degree of accuracy for the determination of hafnium in zirconium (at a limit of $3 \cdot 10^{-3}$%). Nevertheless, in order to attain such success, they had to use a powerful apparatus; thus the spectrograms were photographed in a 6 meter grating spectrograph, using the third order spectra. The dispersion of the spectrograph they used in this instance was 1.6 Å/mm. Using their method, they had to eliminate background resulting from second order cyanogen bands by using a filter (Corning 9863); this filter transmits 90% at 2800 A, but completely absorbs at 4200 A.

For low hafnium concentrations of $3 \cdot 10^{-3}$ to 0.1%, Mortimore and Noble used the analytical pair of spectral lines 2720.2 Å for hafnium and 2820.6 Å for zirconium.

Our aim was to develop a quantitative spectrographic method for determining small amounts of hafnium in zirconium, using a more popular type of apparatus, in particular the ISP-22, which is a spectrograph possessing average dispersion.

1. Selection of Analytical Lines and Conditions for Spectra Excitation

The dispersion of the ISP-22 spectrograph is much lower (12 Å/mm for 2820 Å) than that of Mortimore and Noble's instrument, so that the analytical line of hafnium at 2820.2 Å disappears into the spectral background even at concentrations of ca. 0.1% hafnium, while the zirconium line at 2820.6 A under the conditions we employed was in general not observed. We, therefore, had to choose and test new analytical lines.

To determine small amounts of hafnium, it is essential to choose the most intense lines. The most intense line of hafnium 2641.41 A has the carbon line at 2141.44 A superimposed on it. This is unavoidable since, in order to achieve a high sensitivity, it is necessary to work at high current densities between the carbon electrodes. Moreover, in this part of the spectrum, a strong background is obtained – particularly at high current densities. We found, experimentally, that under our conditions, the 2393.830 A line of hafnium has the greatest sensitivity. In this region, the background is comparatively small. According to results published by the Massachusetts Institute of Technology (MIT) [9], this line should have the Zr II 2393.825 A line of zirconium superimposed upon it. Nevertheless, on removing the hafnium from zirconium, the intensity of the 2393.825 A line was shown to decrease and at concentration of less than 0.01% the line disappeared completely. This, of course, could not occur if there were really a zirconium line at 2393.825 Å. This fact indicates that the MIT workers have wrongly ascribed the hafnium line at 2393.83 A to zirconium, probably as the result of the fact that the preparation of zirconium used by them for recording its lines to complete their tables, still contained traces of hafnium. Confirmation of this supposition was found in the Tables compiled by Gatterer and Junkes [10], in which the 2393.83 Å line found in the zirconium spectrum is ascribed to hafnium. There is also a strong lead line at 2393.794 A, very close to the hafnium line of 2393.83 A. We, accordingly, checked to what extent this line would interfere with hafnium determinations. It was found that traces of lead do not interfere. This is probably a consequence of the fact that most of the lead volatizes during the first 20 seconds of arcing at the high current densities used; 20 seconds is the pre-arc time, i.e., the time during which the sample is in position and the arc is operating, but no photographs are taken. Nevertheless, if the 2393.83 Å line of hafnium is to be used, and the zirconium preparation contains comparatively large amounts of lead, it is recommended that the

lead should be removed beforehand. For determinations of hafnium in amounts greater than ca. 1%, the 2393,83 A line is not suitable, since it falls within the region of overdevelopment of the plate; accordingly a less intense line should be used for concentrations greater than 1%. We chose the line Hf II 2417,61 A; in this case the reference line used was the Zr II 2416,88 A line. The rate at which zirconium and hafnium feed into the discharge space during evaporation of a mixture of oxides from the crater is rather uneven, despite the similarity in physical properties of these two elements. As shown in Fig. 1 this uneveness can be eliminated by mixing the oxides with graphite powder in the ratio of approximately 1:1. Changes in this ratio, even within wide limits, do not affect the relative intensities of the pair of analytical lines.

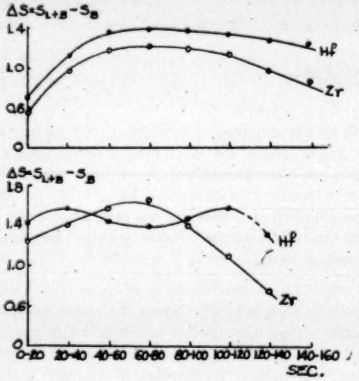


Fig. 1. Zirconium and hafnium feed into the arc from a pure mixture (below) and a mixture with graphite powder (top).

A high current (ca. 15-17 A) is required to evoke the hafnium line at 2393,83 A for concentrations of ~0,01% hafnium. Under these conditions, however, a strong background is obtained, which complicates measurements.

In order to eliminate this background, compounds of the alkali, or alkali-earth elements, are added to the mixture used (test sample + graphite). As a result of preliminary tests, sodium pyrophosphate was chosen as the material to be added, in order to cut down the background to some extent. Fig. 2 illustrates the change in the differences of blackening of the zirconium and hafnium lines, and their relative intensity, respectively, with the percentage of sodium pyrophosphate in the zirconium preparation.

The first points correspond to the blackening of the pure preparation. From Fig. 2 it is clear that only a small amount (20% of the mixture, excluding the graphite) of sodium pyrophosphate is necessary to get maximal differences in blackening. The increase $\Delta S = S_{L+B} - S_B$ is caused mainly, not by an increase in the blackening S_{L+B} but by the decrease in the blackening S_B round the line. (B = background and L = line). Repeated determinations of variations of R with percentage sodium pyrophosphate for samples with a content of ca. 0,05% hafnium showed that for mixtures containing 0 to 15% of pyrophosphate, reproducibility is poor; this is the result of the turbulent burning of the mixtures tested (see curves II and II* on Fig. 2). The relative intensity changes to a comparatively small extent with pyrophosphate concentrations greater than 20%. As a result of preliminary experiments the following ratios were selected: 1 part sodium pyrophosphate to 4 parts of zirconium oxide.

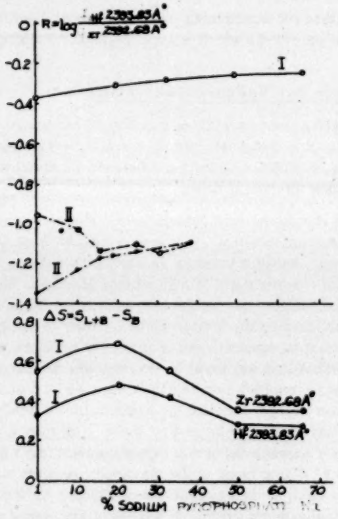


Fig. 2. Relation between the differences in blackening of the zirconium and hafnium lines, and their relative intensity with the percentage of sodium pyrophosphate in the mixture: I) curves for Zr + 0.3% Hf; II) curves for Zr + 0.005 Hf (II* - repeat).

2a. Preparation of Standards

Standards were prepared from the purest zirconium oxide available; this was obtained in the chemistry laboratory as a product of experiments on the separation of hafnium from zirconium. The original hafnium product was hafnium oxide obtained from the "Auer" firm (factory analysis gave 92,2% hafnium*). The hafnium oxide was dissolved in sulfuric acid on boiling. After a 20 minute boil, the solution was cooled and diluted with water.

When an insoluble residue was left it was filtered off and washed; the amount of this residue was determined and the original weight of hafnium corrected by taking into account this insoluble part.

* Checking of this preparation is discussed in part b of this section.

Zirconium oxide purified from hafnium was dissolved in a similar manner in sulfuric acid. From the solutions of $Hf(SO_4)_2$ and $Zr(SO_4)_2$ obtained, solutions of known concentrations were prepared and standard solutions made by mixing these in various proportions.

Mixtures of zirconium and hafnium hydroxides were prepared from the standard solutions by precipitation with ammonia, and then calcined to the oxides at 900° for one hour. The mixed oxides were ground in an agate mortar. Standard samples of the following concentration were prepared:

Standard No.	% of hafnium in the zirconium oxide	Standard No.	% of hafnium in the zirconium oxide
I		VI	0.1
II	0.005	VII	0.3
III	0.01	VIII	1.0
IV	0.02	IX	3.0
V	0.05	X	10.0

2b. Semi-Quantitative Estimation of the Zirconium Content of the Original Hafnium Preparation

According to the "Auer" factory analysis, the original hafnium preparation contained 92.2% hafnium. Quantitative spectrographic analysis of this preparation showed that, apart from the chief impurity —zirconium— there were also present 20 other elements. The small amount of hafnium at our disposal did not permit accurate quantitative determination of the zirconium. It was decided, therefore, to estimate the amount of zirconium in the hafnium at least semi-quantitatively, and for this purpose, the reproduction of a hafnium spectrum in the "Atlas der Restlinien" of Gatterer and Junkes [11], was used. The hafnium preparation, whose spectrum is reproduced in the "Atlas" contained ca. 3% zirconium. On the basis of a comparison of the ratio of the intensities of the 3138.68 Å line of zirconium to the 3139.67 Å hafnium line in the spectrum given in the "Atlas", with the ratio of the intensities of the same lines in the spectrum of our preparation, we concluded that our preparation contains approximately twice the amount of zirconium as the Gatterer and Junkes' sample, i.e., the hafnium oxide from the "Auer" firm contains ca. 6% zirconium. Estimation of the sum of the other impurities gave a value of ca. 2%, so that the sum of all the impurities including zirconium amounts to 8%, a result which is in good enough agreement with the results of the "Auer" firm.

TABLE 1

Operating Conditions Used for Photographing the Spectra

Analytical pair of lines used	$\frac{\text{Hf II } 2393.83\ \text{Å}}{\text{Zr II } 2392.68\ \text{Å}}$ $\frac{\text{Hf II } 2417.69\ \text{Å}}{\text{Zr II } 2416.88\ \text{Å}}$
Concentration ranges	From 0.01 to 1.0% and from 0.3 to 10%
Composition of sample arced	4 parts ZrO_2 + 4 parts graphite + 1 part sodium pyrophosphate
Amount of sample arced	ca. 40 mg of the above mixture
Electrodes	Carbon from material supplied by the Kudinovsky Factory; for their shape see Fig. 3.
Interelectrode distance	3 mm
Spectrograph	The ISP-22
Spectrograph slit	0.005 mm
Emulsion	Ilford process
Preliminary arc without sample	30 seconds at 16 A
Arcing with sample	20 seconds
Exposure	30 seconds
Developing	5 minutes at 20° in a two solution developer: 1) 1000 ml H_2O, 9 g hydroquinone, 2 g potassium bromide, 9 g potassium metabisulfate; 2) 1000 ml H_2O, 18 g KOH
Fixing	1 minute rapid acting; 1000 ml H_2O, 300 g sodium thiosulfate, 60 g ammonium chloride
Densimetry	The MF-2 microphotometer
Excitation source	

• Increasing the current beyond this point has no advantages, since it only increases the background and measurements become difficult.

3. Calibration Curves

The standard samples were photographed 3 times each, the conditions used are listed in Table 1. The analytical lines and the surrounding background were measured photometrically on the MF-2 microphotometer. Logarithms of the relative intensities of the analytical pair of lines

$$R_I = \log \frac{I_{Hf\ 2393.83\ Å}}{I_{Zr\ 2392.68\ Å}} \qquad \text{and} \qquad R_{II} = \log \frac{I_{Hf\ 2417.69\ Å}}{I_{Zr\ 2416.88\ Å}}$$

were calculated, taking into account the background, by means of a calculating machine. Details of the construction of the calculating machine used have been published in the literature [12, 13].

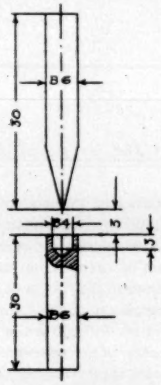


Fig. 3. Carbon electrodes.

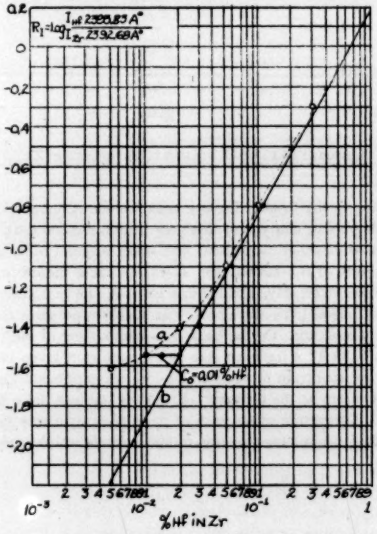


Fig. 4. Calibration curve for the determination of hafnium in zirconium at low concentrations. a) Experimental curve; b) working curve.

The results for R_I and R_{II} were meaned from three measurements. A calibration curve was constructed using these means, within the coordinates ($R_{I,\ II}$, log c_{Hf}). The calibration curves $R_I = f(\log c_{Hf})$ for the concentration range 0.01 to 1.0% and $R_{II} = f(\log c_{Hf})$ for 0.3 to 10% of hafnium in zirconium are shown in Figs. 4 and 5. The experimental curve R_{II} for high hafnium concentration does not bend, but curve R_I, denoted by a, bends slightly at low concentrations. This indicates that the original zirconium material contained some hafnium. By rectifying the curve it was found that the amount of hafnium was ~0.01%. The rectified operating curve on Fig. 4 is denoted by b. The limit of determination of hafnium in zirconium by means of this graph is ~0.01-0.02%.

4. Accuracy and Reproducibility

The accuracy of the results of spectrographic determinations is usually determined either on synthetic mixtures prepared from pure compounds of the test elements, or by comparing the results of two independent methods. In our case, we could not adopt the first method, since the amount of hafnium preparation at our disposal was extremely small, and the second method was out of the question, since, at present, there are no other methods available for analyzing zirconium–hafnium mixtures. In order to check the accuracy of our method, therefore, we analyzed several samples for which it was possible to compile the balance of the absolute amounts of hafnium actually present. This balance was compiled on the basis of spectrographic analysis of the original preparations of zirconium, and of individual fractions obtained from them during fractional distillation of the zirconium in a column as the compound $3ZrCl_4 \cdot 2PCl_5$. Results of tests on the balance are given in Table 2. The original amount of hafnium in samples

TABLE 2

Checking the Accuracy of the Method of Determining Hafnium in Zirconium (Mean values usually obtained from three determinations, rarely from only two determinations).

Original amount of Hafnium			Final amount of hafnium		
Sample No.	% Hf ± the mean error of the mean value	Absolute weight of Hf in g = $m_{Hf_{original}}$	Sample No.	% Hf ± the mean error of the mean value	Absolute weight of Hf in g = $m_{Hf_{original}}$
4009	0.82 ± 0.01	0.984 ± 0.012	4020	1.4 ± 0.15	0.21 ± 0.023
4010	0.50 ± 0.03	0.954 ± 0.057	4021	1.67 ± 0.02	0.167 ± 0.002
4012	0.63 ± 0.03	2.71 ± 0.129	4022	0.96 ± 0.07	0.14 ± 0.01
			4023	0.76 ± 0.04	0.49 ± 0.026
			4024	0.82 ± 0.01	0.05 ± 0.001
			4025	0.98 ± 0.08	0.94 ± 0.077
			4026	0.88 ± 0.02	0.09 ± 0.002
			4027	0.88 ± 0.02	1.02 ± 0.023
			4028	0.75 ± 0.05	0.01 ± 0.001
			4029	0.73 ± 0.06	0.41 ± 0.034
			4030	0.49 ± 0.04	0.02 ± 0.002
			4031	0.50 ± 0.0	0.39 ± 0.00
			4032	0.51 ± 0.01	0.05 ± 0.001
			4033	0.40 ± 0.05	0.21 ± 0.027
			4034	0.62 ± 0.04	0.03 ± 0.002
			4035	0.34 ± 0.04	0.26 ± 0.031
			4035a		0.30

C $m_{Hf_{original}}$ = (4.648 ± 0.198) g

Σ $m_{Hf_{final}}$ = (4.789 ± 0.262) g

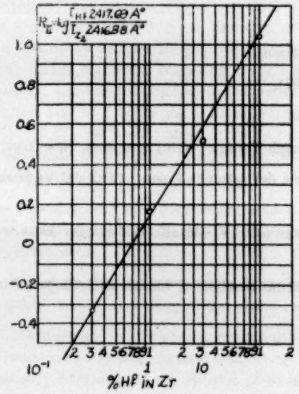


Fig. 5. Calibration curve for determination of hafnium in zirconium at high concentrations.

TABLE 3

Reproducibility of the Results of Determination of Hafnium in Zirconium

Concentration range in % Hf	Mean error of the mean value (in % of the values found)	Number of tests (Total 63)
From 0.013 to 0.05	± 7.5	12
From 0.05 to 0.1	± 5.1	7
From 0.1 to 0.5	± 5.8	11
From 0.5 to 0.1	± 4.5	19
From 0.1 to 5.0	± 7.2	9
From 5.0 to 15	± 6.4	5

numbers 4009, 4010, and 4012 are distributed in the samples from numbers 4020 to 2035a. The results obtained for the original and final amounts of hafnium coincide within the limits of experimental error shown in the table. If it is assumed that the actual amount of hafnium contained in the material of the above experiments is equal to an arithmetic mean of both totals, i.e., 4.72 g hafnium, then the experimental error in the determination of both totals will be equal to only ± 1.5% of this weight.

In order to check on the reproducibility of the results of determinations of hafnium in zirconium, natural mixtures of the oxides of these elements obtained in the chemical laboratory during separation of hafnium from zirconium were analyzed several times. The mean error for the mean values (from three to seven determinations for each sample) shows what the reproducibility of the results is. Table 3 contains the results of the analysis of 63 samples of zirconium containing from 0.013 to 15% hafnium. In general, the possible accuracy and reproducibility satisfy practical requirements for technical and research purposes.

SUMMARY

The spectrochemical methods which are described in the literature for the analysis of hafnium in zirconium are characterized by the use of large and expensive grating spectrographs. The authors of the present work indicate

how they managed to solve the problem of determining hafnium in zirconium using a spectrograph with only average dispersion – the ISP-22; they used a mixture of zirconium and hafnium oxides with powdered graphite and sodium pyrophosphate for evaporation from the crater of the carbon electrodes. The method covers the concentration range 0.01-0.02 to 15% of hafnium in zirconium. The accuracy of the method was checked by balancing up the absolute amounts of hafnium in zirconium test samples; the reproducibility was determined statistically, from the results of analysis of 63 test samples in the concentration range of 0.013 to 15% hafnium in zirconium. Accuracy and reproducibility are both satisfactory.

Received August 2, 1958

LITERATURE CITED

[1] A. Claasen, Z. anal. Chem., 117, 252 (1939).

[2] W. C. Schumb and F. K. Dittman, Ind. Eng. Chem., Anal. Ed., 14, 512 (1942).

[3] D. M. Mortimore and P. A. Romans, J. Opt. Soc. Am., 42, 673 (1952).

[4] A. H. W. Aten, Natuurkunde, 10, 257 (1943).

[5] C. Feldman, Anal. Chem., 21, 1211 (1949).

[6] V. A. Fassel and Ch. H. Anderson, J. Opt. Soc. Am., 40, 742 (1950).

[7] D. M. Mortimore and L. A. Noble, Anal. Chem., 25, 296 (1953).

[8] N. E. Gordon and R. M. Jacobs, Anal. Chem., 25, 1605 (1953).

[9] G. R. Harrison, Massachusetts Institute of Technology Wavelength Tables. Wiley and Sons, New York, 1946.

[10] A. Gatter and J. Junkes, Atlas der Restlinien. Vol. II. Spektren der seltenen Erden. Città del Vaticano, 1945, p. 327.

[11] A. Gatter and J. Junkes, Atlas der Restlinien. Vol. III. Spektren seltener Metalle und einiger Metalloid. Città del Vaticano, 1949. Tabl. 41.

[12] V. K. Prokofiev. "Photographic Methods for Quantitative Spectral Analysis of Metals and Alloys", Part II, State Tech. Press, 1951, p. 194.

[13] H. Kaiser, Spectrochim. Acta., 4, 351 (1951).

COLORIMETRIC DETERMINATION OF VANADIUM BY MEANS OF A CATALYTIC REACTION

V. A. Nazarenko and E. A. Biryuk

Colorimetric methods based on color reactions in which use in made of the fact that the test element can catalytically speed up an oxidation or reduction which is normally slow, are considerably more sensitive than methods based on color reactions which arise purely from complex formation or oxidation. An example of this type is the highly sensitive method for determining rhenium published by N. S, Poluetkov, which is based on the catalytic speed up of the normally slow reduction of stannic chloride by telluric acid in the presence of rhenium [1].

A number of reactions in which vanadium acts as a catalyst have been published by the Hungarian chemists Szebelledy and Ajtai [2]; these reactions are based on the catalytic speed up of the slow oxidation of aromatic amines and aminophenols by chlorate, bromate, or periodate in the presence of vanadium. The catalytic action of vanadium is activated by compounds with which it is capable of forming complex compounds —oxine, pyrocatechol, or tartaric acid. These reactions, according to the above authors, are extremely sensitive. Thus, the reaction between potassium chlorate, and paraphenetidine in the presence of pyrocatechol permits determination of 0.001 γ vanadium (limiting dilution $1:2 \cdot 10^9$), while the reaction between potassium chlorate, aniline, and oxine permits determination of even 0.0001 γ ($1 \cdot 10^{10}$) after standing for 24 hours. The oxidation of paraphenetidine by potassium bromate in the presence of vanadium activated by pyrocatechol has been used for the tempometric determination of vanadium [7].

We studied how these reactions may be used for the colorimetric determination of vanadium, and to what extent the sensitivity of a method based on the catalytic action of vanadium exceeds the sensitivity of the best and most sensitive colorimetric methods based on non-catalytic reactions: the phosphotungstate [3], and benzidine [4], reactions, etc..

We investigated the reaction between potassium chlorate and aniline in the presence of vanadium activated by oxine, which, according to the above authors [2], has the greatest sensitivity.

On adding to 1.5 ml of a neutral solution of sodium or ammonium vanadate, 2 ml of 5% aniline sulfate, 1 ml of saturated potassium chlorate and 0.1 ml of a 1% solution of oxine in 1 N acetic acid, a brownish yellow color gradually develops. In the absence of vanadium a very pale yellow color develops. If this reaction is to be used, therefore, a blank must be made.

The color develops very slowly in the cold; heating accelerates its development. The time for which it is heated is also important: sensitivity increases with prolonged heating. Thus, after 20 minutes at 98-100° (in boiling water) it is possible to detect 0.005 γ vanadium, but after 5 minutes only 0.02 γ. Nevertheless, heating for more than 5 minutes tends to lead to the formation of turbidity and a fine crystalline precipitate in addition to the usual color. After 5 minutes of heating, the solution remains clear. The color which develops on heating the solution increases by an insignificant amount on further standing.

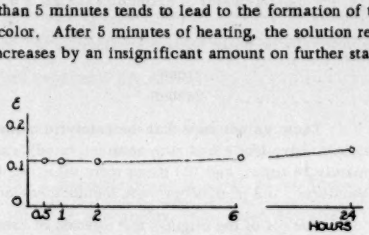


Fig. 1. Relation between color intensity and standing time.

Fig. 1 represents the relation between color intensity and time of standing. The solution contained 0.2 γ vanadium, heating was carried out for 5 minutes. This graph shows that after standing for one hour, the color does not change. A slight increase in color is observed after two hours standing.

Increasing the vanadium concentration leads to an increase in the yellow color, and a series of solutions containing 0.000—0.005—0.010—0.020—0.030—0.05 γ (heating for 20 minutes), or 0.00—0.02—0.05—0.1—0.2 . . . 0.5 γ vanadium (heating for 5 minutes) give a scale of standards which are easily distinguishable visually.

The colors which develop on heating for 5 minutes can be measured on a photometer or photocolorimeter. After a 10 or 20 minute heating period, the colors can only be compared visually, because of the development of

turbidity in solution. For the rest of the work, therefore, we studied the method in which the solution was heated for 5 minutes and the colors were measured on a multi-stage photometer or on the FEK-M photocolorimeter.

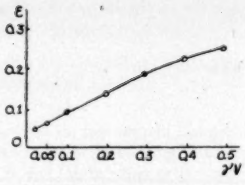


Fig. 2. Relation between color intensity and vanadium concentration.

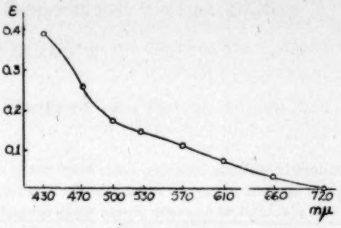


Fig. 3. Absorption curve after heating for 5 minutes.

An absolute straight line relationship is not observed between vanadium concentration and color intensity; this is characteristic in general of reactions based on catalytic effects. Nevertheless, the curve relating color intensity and vanadium concentration, within the concentration limits of 0.02-0.5 γ V, which we studied, is almost indistinguishable from a straight line at the lower concentrations. It is only on the upper part of the curve starting at 0.4 γ that a slight curvature appears. This indicates that this reaction can be used for colorimetric purposes. Extinction was determined against a blank in a 10 mm cell on a multi-stage photometer at 470 mμ.

Fig. 3 represents the absorption curve for a solution containing 0.5 γ vanadium, measured on a multi-stage photometer against water as the blank in a 10 mm cell. Maximum absorption occurs in the short wave side of the visual spectrum and possibly extends into the ultra-violet.

We thought it would be interesting to calculate the apparent (using Tolmachev's term [5]) molar extinction coefficient for the solutions obtained by using this reaction. Naturally, calculation of the true molar extinction coefficient in this case is impossible, since there is no direct proportionality between color intensity and content of the test element in case of catalytic reactions. All the same, the apparent molar extinction coefficient may be used as a characteristic of the sensitivity of this method, if the extinction is referred to the initial concentration of the test element, and the molar coefficient is calculated for a limited segment of the curve by means of the formula

$$\epsilon = \frac{D}{C \cdot l} .$$

The apparent molar extinction coefficient was calculated for the segment 0.1-0.3 γ V on the extinction-vanadium concentration curve, at 430 mμ. For comparison, the apparent molar extinction coefficients were also calculated for the phosphotungstate [6], and benzidene [4], methods. For measurements of extinction against a blank at 430 mμ these coefficients were, respectively,

For the photophotungstate method	1400
For the benzidene method	13000
For the catalytic method	240000

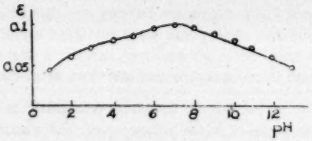


Fig. 4. Relation between color and pH of the original vanadium solution.

These values show that the catalytic method discussed above (for a 5 minute heating period) is approximately 18 times, and 180 times more sensitive than the benzidene, and phosphotungstate methods, respectively.

The pH of the original test solution of vanadium exerts a very strong influence on the intensity of the color developed. The pH should be within the limits 6.5-7.5. If acid solutions are analyzed, they must be first evaporated to dryness, and the residue dissolved in water. Fig. 4 represents the relation between extinction and pH of the original vanadium solution.

TABLE 1

V taken in γ	0	0.05	0.10	0.10	0.15	0.20	0.20	0.30
V found in γ	0	0.05	0.10	0.08	0.15	0.20	0.25	0.30

TABLE 2

No. of test in order	V taken in γ	Added in γ	V found in γ
1	0	Fe 5	0
2	0.05	Fe 5	0.05
3	0.30	Fe 5	0.30
4	0.10	Cu 5	0.10
5	0.20	Cu 5	0.20
6	0.20	Mo 10	0.20
7	0.20	W 10	0.20
8	0.10	Ti 10	0.10
9	0.20	Bi 10	0.20
10	0.20	As 10	0.20
11	0.20	Zr 10	0.20

The method is reasonably specific. The presence in the test solution of up to 10 γ of molybdenum, tungsten, rhenium, titanium, arsenic, antimony, bismuth, zirconium, and aluminum does not interfere with vanadium determination; larger amounts were not tested. Copper in amounts up to 5 γ does not affect vanadium determination. 100 γ copper leads to formation of a color which corresponds in intensity to 0.1 γ of vanadium; the color developed in this case is, however, a greenish one. Iron interferes with vanadium determination; even 2 γ of iron gives a brown-yellow color which corresponds in intensity to 0.05 γ vanadium.

Masking iron with potassium bifluoride [2] does not lead to the required result. 0.2 ml of 0.05% potassium bifluoride cannot mask more than 2 γ iron, but the intensity of the color which vanadium gives rise to is halved. Sodium pyrophosphate proved to be a much better complexing agent. 0.1 ml of a solution saturated in the cold with sodium pyrophosphate masked 10 γ iron, while hardly affecting the vanadium reaction. An increase in the amount of pyrophosphate leads to masking of the vanadium reaction.

Vanadium can, therefore, be determined as follows: to 1.5 ml of test solution (pH 6.5-7.5) is added 0.1 ml of a saturated solution of sodium pyrophosphate, 2 ml of 5% aniline sulfate, 1 ml of a saturated solution of potassium chlorate and 0.1 ml of a 1% solution of oxine in 1 N acetic acid. The solutions are mixed and the test tube containing the mixture immersed in boiling water for 20 minutes (for the determination of 0.005-0.020 γ vanadium) or 5 minutes (for more than 0.02 γ vanadium). The solution is then cooled and the color intensity measured by comparing with standards prepared in the same way. For the determination of 0.02-0.5 γ V it is possible to determine the optical density at 430-470 mμ, using the FEK-M photocolorimeter with a blue light filter. The amount of vanadium in this case is found from the calibration curve.

Table 1 contains some of the results obtained during the determination of vanadium by the catalytic method, by measuring the extinction on a multi-stage photometer against a blank and using a calibration curve. Table 2 contains results of vanadium determinations in the presence of certain metals.

The results included in these tables show that the reaction based on the catalytic speed up of the oxidation of aniline by chlorate in the presence of vanadium activated by oxine, can be used for the colorimetric determination of amounts of vanadium which cannot be determined by other colorimetric methods.

SUMMARY

1. A reaction based on the catalytic speed-up of the oxidation of aniline by chlorate in the presence of vanadium activated by oxine, may be used for the colorimetric determination of submicrogram quantities of vanadium.

2. A colorimetric method based on this reaction permits determination of 0.005-0.5 γ vanadium.

Received September 27, 1954

LITERATURE CITED

[1] N. S. Poluetkov, J. Appl Chem., 14, 695 (1941).

[2] L. Szebelledy and M. Ajtai, Mikrochemie, 25, 258 (1938); 26, 72, 75 (1939).

[3] A. P. Vinogradov, Proc. Acad. Sci. USSR, 1931 A, 249.

[4] I. P. Alimarin, J. Appl. Chem., 17, 83 (1944).

[5] V. N. Tolmachev, Scientific Reps. of Kharkov University, 37, 65 (1951).

[6] E. B. Sendel, "Colorimetric Determination of Traces of Metals", State Chem. Press, 1949, p. 161.

[7] L. Szebelledy and M. Ajtai, Mikrochemie, 26, 87 (1939).

BLANK
PAGE

ORGANIC COPRECIPITANTS

2. COPRECIPITATION OF TUNGSTEN WITH ORGANIC COPRECIPITANTS*

V. I. Kuznetsov, M. N. Obozhin and E. S. Palshin

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry Acad. Sci. USSR, Moscow

According to published results, tungsten can be fairly completely precipitated, without using special precipitants, from acid solutions in which the tungsten concentrations are not too low, and which do not contain chlorides [1, 2]. For low tungsten concentrations or in the presence of chlorides, special precipitants must be used to ensure complete precipitation of tungsten.

A large number of precipitants have been described in the literature for tungsten, the majority of them being amines of various types. Among those recommended are cinchonine, which was proposed as far back as 1895 by Gremer [3], quinine [4], totaquine [5], brucine [6], and other alkaloids, or mixtures of them, the sometimes so-called "alkaloid residues"; benzidene [7], α-naphthylamine [8], 8-toluquinaldine [9], β-naphthoquinoline [10, 11], nitron [12], pyramidone [13], tetramethyl-p-diaminodiphenylmethane [14], rhodamine B [15], sulfamido-2,4-diamino benzene [16], hexamethylenetetramine [17], piperazine [18], tetramethyl diaminobenzophenone [19], vanillidenebenzidene [20], p-aminoisopropylbenzene [19], 8-hydroxyquinoline [21, 33], anti-1,5-di(p-methoxyphenyl)-1-hydroxylamino-3-hydroxylamino-4-pentene [22], α-benzoinoxime [23, 26], tannin [24], gelatin [25, 26], and others, information about which may be obtained from detailed reviews [27, 28].

We were interested in checking the suitability of the recommended precipitants for precipitating tungsten from very dilute solutions. For convenience of comparing the action of various precipitants, we carried out all precipitations under approximately identical conditions. The following conditions were employed. To 100 ml of water was

TABLE 1

Precipitation of Tungsten from Dilute Solutions by Means of Organic Precipitants

Precipitant	% of the amount of tungsten added which is actually precipitated		Literature cited
	$1:2\cdot10^5$	$1:10^6$	
Nitron	76^D	47^D	[31]
Methylene Blue	–	28.2	[39]
p-Dimethylaminoazobenzene	–	23	–
Antrazo[anthraquinone-(1-azo-4)-dimethylaniline]	–	21	–
Rivanol	–	10.6	–
Methylviolet	–	12	–
Benzidene hydrochloride	10	6.5	[32]
Gelatin	–	6	[25]
8-Hydroxyquinoline	9^D	3.3^D	[33]
Michler's ketone (tetramethyldiaminobenzophenone)	24.4	2.3	[13]
Tannin	5.5	2^D	[23]
Pyramidone	–	1.3^D	[12]

Note: In the experiments denoted by D, the solutions were allowed to stand for 6-12 hours before filtration.

added 100 γ tungsten as Na_2WO_4 containing radioactive W^{185}, the solution was carefully mixed, acidified with hydrochloric acid to a normality of 0.03 N, and a small amount of macerated paper introduced – the same amount in each case – and finally the test precipitant. The amount of precipitant added was approximately the same in each case. After standing for one hour, the solution was filtered through a filter paper (blue ribbon quality), the precipitate washed slightly with a wash liquor containing the precipitating agent, the filter paper plus precipitate was then dried and ashed

* The first part of this communication was published in J. Anal. Chem., 9, 199 (1954). [See C. B. Translation, page 224].

at a temperature not greater than 700° [29, 30], and the amount of coprecipitated tungsten determined radiometrically using the usual type of β-particle counter. The amount of W^{185} added in each instance corresponded to an activity of 1300 impulses/minute. The background amounted to 12-14 impulses/minute. Screening was taken into account in the usual fashion. The results obtained are adduced in Table 1.

These results show that even at dilutions of tungsten of 1:200,000 complete precipitation of tungsten is not achieved when precipitants normally recommended are used.

This incomplete precipitation of tungsten when the usually recommended precipitants are used has already been pointed out by a few authors [34, 35].

As a preliminary to concentrating the tungsten in order to increase the completeness with which it is precipitated, it has been suggested that molybdenum should be added to the solution and that the tungsten be then coprecipitated with molybdenum by the action of α-benzoinoxime [36]. It is, however, more convenient to coprecipitate tungsten with an organic coprecipitant which can afterward be readily removed by simple ignition, rather than with molybdenum.

Organic Coprecipitants for Tungsten

The general chemical theory underlying the action of organic coprecipitants which has been outlined previously [40], indicates how to look for suitable coprecipitants for many elements, including tungsten. According to the hypothesis advanced in that article, one would expect that tungsten could be satisfactorily precipitated as the respective tungstates by means of heavy organic bases. For coprecipitation of these tungstates it should then be possible to use any sparingly soluble salt of the same organic bases.

Experiments carried out, however, showed that during attempts to coprecipitate tungstates in this way, even at a dilution of tungsten of 1:200,000,000 only 30-40% of tungsten is coprecipitated. Results such as this were observed when a combination of benzidene and salts of anthraquinone-α-sulfonic acid was used, i.e., on coprecipitation of tungsten with precipitates of benzidene anthraquinone-α-sulfonate, on coprecipitation with precipitates formed between Methyl Violet and the sulfonic acids of poly azo compounds, and for other combinations.

A study of the mechanism of coprecipitation of tungsten showed that the reason for this incomplete coprecipitation is not the fault of the coprecipitant as such, but that it is a consequence of the nature of those ions and particles in which tungsten is present in acid solutions. It is well-known that after acidification of alkaline solutions of normal tungstates, tungsten is present in the acid solution thus formed, not only as WO_4^{2-} ions, but also in the form of various anions of tungsten isopoly acids, and also in the form of colloidal particles. The characteristics of the precipitation of tungsten from acid solution are also explicable by the above effect.

Thus, Shu Chuan-Liang and Kan Nan-Chang [41], while investigating the precipitation of tungsten with benzidene (Bzd), and determining the ratio of benzidene:tungsten in the precipitate, found that no normal tungstates of the composition $(Bzd)H_2WO_4$ was precipitated from acid solutions. The lower the pH, the smaller the ratio benzidene : tungsten; the following ratios were observed:

pH	Ratio Bzd : WO_3
3.61	1:1.99
4.43	1:1.43
5.15	1:1.24

Platunov [40], while studying precipitation of tungsten with methylene blue and with salts of other organic bases, also turned his attention to the fact that precipitates of tungsten from solutions containing tungsten in various forms, —in the form of normal, p- or m-tungstates— is irregular. When tungsten is present as colloidal particles, its precipitation takes a different course from that it takes when tungsten is present in the form of anions. The mechanism considered above is not applicable to the precipitation of tungsten in a colloidal form; in this case, it is a question of colloidal-chemical precipitation. Since tungsten is simultaneously present in solution in the form of particles and ions of varying nature, it is obvious, that complete coprecipitation of tungsten cannot be achieved by a coprecipitant which acts only according to one mechanism. It is essential, therefore, to use more than one coprecipitant, which acts according to different mechanisms.*

* B. A. Platunov approaches this question from another angle. He reckons that a coprecipitant is a good one when it precipitates tungsten in the form of both normal, and m- and p-tungstates fairly completely [39].

After trying a few combinations, we found that complete precipitation of tungsten could be achieved even from very dilute solutions by using a mixture of Methyl Violet and tannin.

The use of a mixture of organic precipitants for precipitation of tungsten, in particular from special mixtures containing tannin, has been described long ago [34, 37, 38]. Nevertheless, we are not aware of any work which emphasizes the exceptional significance of such mixtures for the complete precipitation of tungsten from very dilute solution. Thus, in one of the most recent papers by B. A. Platnuov on the application of mixtures containing tannin, although it is pointed out that tannin improves the completeness of tungsten precipitation, he does not emphasize that such mixtures are capable of precipitating tungsten from very weak solutions [39]. In these experiments of Platunov, the greatest dilution employed was only 1:10,000.

Coprecipitation of Tungsten from Very Dilute Solutions by Means of a Mixture of Methyl Violet and Tannin

Coprecipitation was studied by carrying out the following experiments. To 100-200 ml of water was added microgram amounts of tungsten as Na_2WO_4 containing radioactive W^{185}; the mixtures were acidified with hydrochloric acid to 0.2 N, and then precipitant either added immediately, or after preliminary heating on a boiling water bath. Macerated paper was first added; this was followed by an aqueous solution of 50 mg tannin and 10 ml of a 1% aqueous solution of Methyl Violet. After standing for 20 minutes, the dark violet precipitate was filtered off, slightly washed with an acidified solution containing Methyl Violet and tannin. It was then dried and ashed at a temperature not greater than 700°. The amount of coprecipitated tungsten was determined radiometrically in the residue.

TABLE 2

Coprecipitation of Tungsten with a Mixture of Methyl Violet and Tannin from 0.2 N Hydrochloric Acid Solutions

Dilution of tungsten	Tungsten		% of Tungsten coprecipitated
	amount taken in γ	amount found in γ	
1: 200,000,000	1.00	1.00	100
1: 1,000,000,000	0.20	0.19	96
1:10,000,000,000	0.18	0.183	102

TABLE 3

Separation of Coprecipitated Tungsten from Other Elements (Precipitation was carried out from a volume of 100 ml, the dilution of the tungsten was $1:10^8$).

Element present, in mg		Ratio – element present : W	Tungsten		Coprecipitation	
			taken, in γ	found, in γ	tungsten, in %	other elements, in %
Aluminum	1 mg	1: 1,000	1.00	0.96	99	
"	10 mg	1: 10,000	1.00	1.00	100	
"	100 mg	1:100,000	1.00	1.01	101	< 0.3
Calcium	1 mg	1: 1,000	1.00	0.97	97	
"	10 mg	1: 10,000	1.00	0.97	97	
"	100 mg	1:100,000	1.00	0.96	96	< 0.3
Magnesium	1 mg	1: 1,000	1.00	0.96	96	
"	10 mg	1: 10,000	1.00	0.97	97	
"	100 mg	1:100,000	1.00	0.95	95	< 0.3
Silicon	1 mg	1: 1,000	1.00	0.98	98	80
"	10 mg	1: 10,000	1.00	0.99	99	15
"	100 mg	1:100,000	1.00	1.00	100	2.4

The results obtained, which are given in Table 2, show that by carrying out coprecipitation in this way, it is possible to coprecipitate tungsten completely, even from solutions at dilutions of $1:10^{10}$, which corresponds to tungsten concentration of $5 \cdot 10^{-10}$ mol/liter. The presence of chlorides or hydrochloric acid in this case, does not impair the completeness with which tungsten is precipitated.

Experiments which we carried out on precipitation of tungsten with a mixture of tannin and Methyl Violet as recommended by Platunov [39], showed that at dilutions of tungsten up to $1:10^8$, this mixture gives complete precipitation of tungsten. During our experiments it became clear that considerably smaller amounts of tannin can be used. Working with a volume of 200 ml of solution, as Platunov did, we got 100% precipitation of tungsten using only 0.1 g of tannin instead of 0.5-2 g as recommended by Platunov.

Selectivity of Coprecipitation

This work was only carried out to show that by using reliably chosen organic coprecipitants it is possible to get complete coprecipitation of tungsten.

Since tannin in acid media is itself a precipitant for several elements, e.g., titanium or zirconium, it is obvious that from the point of view of selectivity tannin is not an ideal ingredient of an organic coprecipitant for tungsten. By coming to an understanding of the mechanism of the action of a coprecipitant it should be possible to select other ingredients more suitable than tannin + Methyl Violet. In the absence in solution, of elements precipitated by tannin, the coprecipitants described ensure complete coprecipitation of tungsten with simultaneous separation from a number of other elements which are not precipitated.

We adduced, therefore, results on the separation of tungsten from other elements which were carried out in exactly the same way as for coprecipitation of tungsten from pure solutions (Table 3). We did not succeed in separating tungsten from titanium and molybdenum by using mixtures containing tannin.

SUMMARY

Individual precipitants which have been recommended for tungsten, such as nitron, cinchonine, quinine, and many others, do not ensure complete precipitation of tungsten even at dilutions of tungsten of $1:2 \cdot 10^5$. Complete precipitation of tungsten from acid solutions cannot be achieved by using any one precipitant, since tungsten is present in acid solution in the form of ions of various types and also as colloidal particles. To precipitate tungsten completely, it is essential to use a mixed precipitant which works in virtue of both chemical and colloidal-chemical precipitating properties. Such mixtures have already been described in the literature (B. A. Platunov, etc.), but no emphasis was laid on the exceptional significance of such mixtures for ensuring complete precipitation of tungsten from very dilute solution.

By using a mixture of Methyl Violet and tannin, complete coprecipitation of tungsten can be achieved at dilution of $1:10^{10}$ with simultaneous separation from Ca, Mg, Al and a number of other elements.

Received August 27, 1954

LITERATURE CITED

[1] Yu. A. Chernikhov and V. G. Goryushina, Factory Labs., 12, 518 (1946).

[2] M. A. Popov, Factory Labs., 13, 379 (1947).

[3] F. Gremer, J. Eng. Min., 59, 345 (1895).

[4] L. Lefort, Chem. News, 45, 57 (1882); G. Gutzeit, Helv. chim. Acta., 12, 713 (1929).

[5] P. Philipp, Chem. Abs., 42, 6268 (1948).

[6] F. S. Grimaldi, Norman Davidson, U. S. Geol. Survey; Bull. No. 950, 135 (1946); Chem. Abs., 41, 49 (1947).

[7] G. Knorre, Ber., 38, 783 (1905).

[8] M. Tshilikin, Ber., 42, 1302 (1909).

[9] R. B. Golubtsova, F. M. Shemyakin, Proc. Commission on Anal. Chem., 3, 241 (1951).

[10] B. A. Platunov, Papers of Leningrad University, 12, 101 (1947).

[11] B. A. Platunov and N. M. Kirillova, Scientific Reps. of Leningrad University, Chem. Series 54, 269 (1940); Chem. Ref. Journal, 4,73 (1941).

[12] A. Gutbier, G. Weise, Z. anal. Chem., 53, 426 (1914).

[13] S. I. Gusev and V. I. Kumov, J. Anal. Chem., 3, 373 (1948).

[14] M. Papafil, R. Cernatesco, Ann. Sci. Univ. Jassy, 16, 526 (1931); J. H. Yoe and L. A. Sarver, Organic Analytical Reagents, 1941.

[15] I. T. Oats, J. Eng. a. Min., 144, 72 (1943).

[16] V. V. Fomin, V. V. Shalyagin and V. G. Starostina, Factory Labs., 6, 679 (1947).

[17] Vivario, Pharm. weekblatt., 54, 157 (1917) according to S. I. Gusev and V. I. Kumov, J. Anal. Chem., 3, 373 (1948).

[18] A. Martini, Microchemie, 6, 63 (1928).

[19] E. Kofka, Z. anal. Chem., 52, 601 (1913).

[20] Y. Hovorca, Chem. listy, 33, 212 (1939).

[21] S. Halberstadt, Z. anal. Chem., 92, 86 (1932).

[22] J. H. Yoe, A. L. Jones, Ind. Eng. Chem., Anal. Ed., 16, 45 (1944).

[23] H. Yacoda, H. Fales, J. Am. Chem. Soc., 60, 640 (1938).

[24] D. A. Lambie, Analyst, 70, 124 (1945).

[25] Weiss and Sieger, Z. anal. Chem., 119, 245 (1940).

[26] N. A. Tananaev and M. N. Lotsmanova, J. Anal. Chem., 1, 206 (1946).

[27] Yu. A. Chernikhov and V. G. Goryushina, Factory Labs., 6, 520 (1946).

[28] F. Ubeda, E. Gonzales, Herrera dela Sota, Chem. Abs., 41, 4060 (1947).

[29] T. Millner, J. Neugebauer, Nature, 163, 601 (1949).

[30] Shu Chuan-Liang, Science Record (Shanghai) 2, 366 (1949); C. A. 46, 950 (1952).

[31] F. J. Welcher, Organic Analytical Reagents, New York, 1949, III, p. 138.

[32] F. J. Welcher, Organic Analytical Reagents, New York, 1948, I, p. 312.

[33] R. Berg, "Application of 8-Hydroxyquinoline in Analytical Chemistry", State Sci. Tech. Press, 1937.

[34] W. R. Shoeller and C. Jahn, Analyst, 52, 504 (1927).

[35] F. W. Box, Analyst, 69, 272 (1944).

[36] P. Fischer, R. Spiers, P. Lisan, Ind. Eng. Chem., Anal. Ed., 16, 607 (1944).

[37] L. Moser and W. Blaustein, Monatsh., 52, 353 (1929).

[38] B. A. Platunov, Reps. of Leningrad University, 12 (1947), p. 10.

[39] B. A. Platunov and A. E. Diech, Reps. of Leningrad University, 9, 199 (1954).

[40] V. I. Kuznetsov, J. Anal. Chem., 9, 199 (1954).*

[41] Shu Chuan-Liang and Kan Nan-Chang, J. Chinese Chem. Soc., 18, 31 (1951); Chem. Abs., 46, 950 (1952).

* See Consultants Bureau Translation, page 224.

BLANK
PAGE

POTENTIOMETRIC TITRATION USING THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE ON A PLATINUM ELECTRODE

I. E. Flis

The V. M. Molotov Leningrad Institute of Technology

Potentiometric analysis of many systems, the state of which depends on hydrogen ion activity, may be realized by using an electrode obtained by catalytic decomposition of hydrogen peroxide on platinum.

The experimental technique of such a potentiometric titration is not complicated. In practice, all it boils down to is that 2-3 ml of a 3% solution of hydrogen peroxide is added to the test solution and a platinum plate or grid immersed in it. Oxygen is thereupon liberated on the platinum. Our experiments showed that the potential of such an electrode changes regularly with changes in the pH of the solution; potentiometric titration of acids, bases, and certain salts is, accordingly, possible by means of this electrode.

In order to check on the relation between the potential of the electrode under discussion and hydrogen ion activity, measurements were carried out in a series of buffer solutions.

Before titration, the hydrogen ion activity of each solution was measured with a hydrogen electrode; the potential of the platinum electrode on which oxygen was evolved as a result of the catalytic decomposition of hydrogen peroxide was then measured. The results are given graphically in Fig. 1.

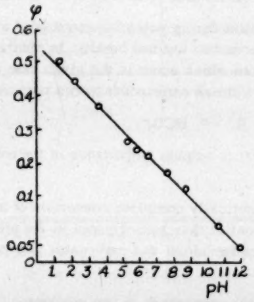


Fig. 1. Relation between electrode potential and pH.

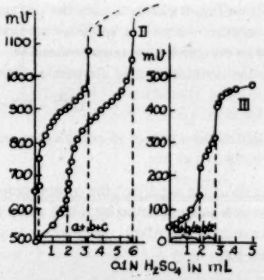


Fig. 2. Potentiometric titration curves for alkali, carbonates, and hypochlorite in solution.

The graph in Fig. 1 shows that the potential of the electrode described varies linearly with pH.

$\frac{d\varphi}{d\,pH}$ amounts to approximately 0.055 V/pH unit.

The E.M.F. values given in Fig. 1 were measured relative to the saturated calomel electrode. It is, therefore, necessary to add 0.25 V to these values if they are to be referred to the hydrogen potential as zero. It is evident that the potential of the electrode under discussion does not coincide with the usual potential of the oxygen electrode; it is approximately 0.4 V lower. The electrode described cannot, therefore, be accepted as an oxygen electrode in the usual sense.

Despite this, the experimental results represented on Fig. 1 show that it can still be used for potentiometric titrations which are based on changes in the concentration or activity of hydrogen ions in solution.

Titration using the decomposition of hydrogen peroxide on platinum can be applied to certain cases where the hydrogen and quinhydrone electrodes are inapplicable; sometimes it can even be used as a substitute for titration with a glass electrode. As an example, we have described below its application to the analysis of hypochlorite and chlorite solutions.

Solutions of hypochlorites which are widely used at present for various oxidation processes, in particular, for bleaching cellulose and fabrics, always contain a certain amount of free alkali and sometimes carbonates as well.

The rate and quality of cellulose and fabric bleaching depends to a considerable extent on the pH of the bleaching solutions. The pH values and the changes in pH which occur during bleaching are naturally a function of the alkali and carbonate concentrations. Determination of the latter is, therefore, essential. Present day chemical methods [1, 2], do not permit separate determination of alkali and carbonate in hypochlorite solutions with sufficient accuracy. The same is true of the potentiometric method suggested by Abribat [3].

Potentiometric titration of hypochlorite solutions with acid permits accurate determination of the active chlorine and alkali contents [4]. In the absence of carbonates, such an analysis can be carried out by simple potentiometric titration of the solution with sulfuric acid, using a platinum grid or plate electrode, which in this instance acts as an oxidation-reduction electrode.

The potential of such an electrode varies uniformly with pH changes which occur during titration of hypochlorite solution with acids [4]. The change of potential of such a platinum electrode is shown in Fig. 2, Curve I. Two sudden potential changes are evident on this curve. The small part of Curve I preceding the first break corresponds to a neutralization of the free alkali formed in solution:

$$OH^- + H^+ \rightarrow H_2O.$$

The part of Curve I lying between the first and second breaks corresponds to the process: $ClO^- + H^+ \rightarrow HClO$.

The vertical dotted lines projected onto the abscissa from these two breaks make intercepts which corresponds to the number of ml's of acid used to neutralize the alkali, and to react with the hypochlorite respectively. It is possible thereby to calculate the alkali and hypochlorite content of a test mixture with reasonable accuracy.

Curve II on Fig. 2 characterizes the change in the relative potential during potential titration of a sodium hypochlorite solution containing sodium carbonate and alkali. This curve also has two breaks. In contrast to Curve I, the first break on Curve II is rather extended. Analysis of the reactions which occur in the given case during titration leads to the conclusion that the part of Curve II preceding the first break corresponds to two processes:

$$OH^- + H^+ \rightarrow H_2O \text{ and } CO_3^{2-} + H^+ \rightarrow HCO_3^-.$$

The latter reaction does not go to completion, since a new process starts to acquire importance in the solution: $ClO^- + H^+ \rightarrow HClO$.

As a result of the superposition of one process on another, the practically complete conversion of a carbonate into bicarbonate is accompanied by a less sharp change in relative potential than was observed in the previous case after neutralization of the alkali. It is accordingly impossible to determine alkali and carbonates in hypochlorite solution in this way.

The part of Curve II which lies between the first and second breaks corresponds to two processes:

$$ClO^- + H^+ \rightarrow HClO \text{ and } HCO_3^- + H^+ \rightarrow H_2CO_3(CO_2 + H_2O).$$

The vertical dotted line which is projected from the point of the second break onto the abscissa makes an intercept which corresponds to the number of ml's of acid used to neutralize the alkali, for interaction with sodium carbonate, and for the reaction with hypochlorite.

Let us denote the number of ml's of acid used to neutralize free alkali by a; the ml's of acid used in the reaction with carbonate, and hypochlorite by b and c, respectively. Then the number of ml's corresponding to the intercept made by the dotted perpendicular line drawn from the point of the second break of Curve II onto the abscissa will be $(a + b + c)$.

To determine a, b and c it is necessary to carry out a second titration, which is easily done by means of the electrode described above. To do this, a 3% solution of hydrogen peroxide is added to the test solution in such amount that after decomposition of the hypochlorite: $ClO^- + H_2O_2 \rightarrow Cl^- + H_2O + O_2$ there still remains 2-3 ml of hydrogen peroxide in solution. After decomposition of the hypochlorite, a platinum grid or plate is lowered into the solution. Oxygen is then evolved at the electrode. The alkali and sodium carbonate which remain in the test solution are now titrated potentiometrically with acid.

Curve III, Fig. 2 illustrates the potential change of such an electrode during titration of a second sample of the test solution with acid, after decomposition of the hypochlorite with excess hydrogen peroxide. Two sharp breaks are visible on Curve III. The part of the curve preceding the first break corresponds to the processes:

$$OH^- + H^+ \rightarrow H_2O \text{ and } CO_3^{2-} + H^+ \rightarrow HCO_3^-.$$

Consequently, the dotted line projected from the point of the first break on to the abscissa makes an intercept equal to $\underline{a} + \frac{\underline{b}}{2}$ ml's of acid.

The part of the curve which lies between the first and second breaks corresponds to the process:

$$HCO_3^- + H^+ \rightarrow H_2CO_3(CO_2 + H_2O).$$

The dotted line projected from the point of the second break on to the abscissa makes an intercept equal to ($\underline{a} + \underline{b}$) ml's of acid. By combining the results of the first and second titrations, it is not difficult to calculated $\underline{a}$, $\underline{b}$ and $\underline{c}$, thereby determining the contents of alkali, sodium carbonate, and active chlorine, respectively in a test solution.*

In order to check the proposed method, we made a series of experiments by means of which it was possible to compare the results of determinations of hypochlorite in solution by the potentiometric method described above with results of iodometric analysis

Some of the results which were obtained are adduced in the following table.**

Hypochlorite equivalent (iodometric method)	Acid equivalent according to the first titration	Bicarbonate equivalent by potentiometric titration	Alkali equivalent by potentiometric titration	Hypochlorite equivalent by potentiometric titration
0.00720	0.01360	0.00500	None	0.00720
0.00705	0.01360	0.00505	None	0.00700
0.00780	0.00430	None	0.00035	0.00790
0.00575	0.00320	None	0.00030	0.00580
0.00590	0.00580	0.00095	0.00095	0.00590
0.00590	0.00575	0.00095	0.00095	0.00585

The data given in the table show that the results of potentiometric and iodometric determinations are in reasonably good agreement for hypochlorite contents. This indicates that the potentiometric method suggested is reliable. The platinum electrode may also be used for direct determination of alkali and sodium carbonate in chlorite solutions; in this case, it fully replaces the glass electrode, since here the hydrogen and quinhydrone electrodes cannot be used.

Chlorites are usually prepared by the reaction of chlorine dioxide with peroxides in alkaline solution. The chlorite solution thus prepared, therefore, usually contains alkali and carbonates. For bleaching cellulose and fabrics these solutions are acidified to a definite pH. Bleaching is usually carried out in a weak acid medium (pH ≈ 5-4).

Since the presence of alkali and carbonates confers buffer properties on the solution, it follows that the amount of acid which has to be added (to get the requisite pH) depends on the content of alkali and carbonate in solution. The determination of the latter is, therefore, an essential element in analyzing chlorite bleaching solutions.

Potentiometric analysis of alkali and carbonates in chlorite solution can also be carried out by means of the method suggested. In contrast to hypochlorites, chlorites hardly react at all with hydrogen peroxide. The hydrogen peroxide added in such cases, therefore, only serves as an oxygen source.

The galvanic circuit used was the following:

Pt	Test solution (H_2O_2)	KCl saturated solution	KCl saturated HgCl	Hg ;

test solution was titrated with acid.

* To determine the oxygen equivalent of the hypochlorite, $\underline{c}$ must be doubled. The values of $\underline{a}$, $\underline{b}$ and $\underline{c}$, naturally, may also be expressed as number of equivalents.

** M. K. Bynyaeva helped in this part of the work.

In order to check on this method a series of parallel potentiometric titrations was made using this particular technique and also using a glass electrode.

Figs. 3 and 4 represent the results of titration of alkaline solutions of sodium chlorite with acid.* The experimental results obtained using the two electrodes are practically coincident. This shows that in the given instance the electrode formed by decomposition of hydrogen peroxide on platinum may be used instead of a glass electrode. The dotted line projected on to the abscissa in Fig. 3 makes an intercept which corresponds to the amount of ml's of acid expended in neutralizing the alkali in the test solution.

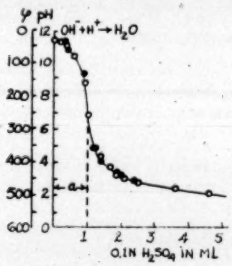


Fig. 3. Potentiometric titration curves for alkaline solutions of chlorite not containing carbonate: o = titration with a glass electrode; • = titration with the test electrode.

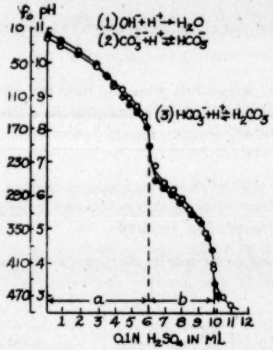


Fig. 4. Potentiometric titration curves for alkaline solutions of sodium chlorite containing carbonate: o = with a glass electrode; • = with the test electrode.

The dotted line projected from the point of the first break on the curve in Fig. 4 on to the abscissa makes an intercept which corresponds to the number of ml's of acid used to neutralize free alkali and conversion of carbonate to bicarbonate (intercept a). The dotted line projected on to the abscissa from the point of the second break on these curves, makes an intercept which corresponds to the number of ml's of acid used to neutralize the alkali and for reacting with sodium carbonate (a + b).

By means of these curves it is thus possible to calculate the individual amounts of free alkali and sodium carbonate in test chlorite solutions. Potentiometric titration by means of the technique described can be carried out on an ordinary potentiometric titration set-up [5, 6, 7].

A platinum plate or grid can be used as the electrode. The platinum electrode used for measuring pH with the quinhydrone electrode is suitable. Apparatus used for ordinary potentiometric titration and manufactured in Russia can be used. The technique described can, therefore, be used in any factory laboratory.

SUMMARY

1. An electrode is described which is obtained by the catalytic decomposition of hydrogen peroxide on platinum when oxygen is evolved.

2. A potentiometric method has been developed for the analysis of active chlorine, alkali, and sodium carbonate in hypochlorite solutions, and also a method for the determination of alkali and sodium carbonate in chlorite solutions using the same type of electrode.

3. The regular change of electrode potential with pH changes means that this electrode may find possible uses for potentiometric analysis in many other instances.

Received October 26, 1953

LITERATURE CITED

[1] A. Pakshver, Factory Labs., 8, 803 (1939).

[2] M. K. Mokoshev, "Analysis and Prevention of Flaws in Finishing Cotton Fabrics", State Light-Industry

Press, 1947, p. 238.

[3] M. Abribat, Bull. Soc. chim. France, 49, No. 8 (1931).

[4] B. P. Nikolsky and I. E. Flis, J. Gen. Chem., 22, 1298 (1952)* see also "Proc. Leningrad Tech. Inst.", 1, 1949, p. 61.

[5] B. P. Nikolsky, Articles in the Symposium "Contempory Physico-Chemical Methods of Chemical Analysis", State Chem. Tech. Press, 1932, p. 7.

[6] N. Kolthoff and N. Furman, "Potentiometric Titration", State Sci. Tech. Press Chem. Theory, 1934.

[7] H. T. Britton, "Hydrogen Ions", State Sci. Tech. Press, Chem. Theory, 1933.

* See Consultants Bureau Translation, p. 1343.

BLANK
PAGE

POTENTIOMETRIC DETERMINATION OF $Cr_2O_7^{2-}$ IONS AND STRONG ACIDS WHEN BOTH ARE PRESENT SIMULTANEOUSLY

I. E. Flis and Zh. L. Vert

The V. M. Molotov Leningrad Institute of Technology

No satisfactory method has hitherto been described in the literature for the analysis of solutions of sexivalent chromium in sulfuric and nitric acids, which are widely used technically.

In order to determine the components of the system $H_2SO_4-K_2Cr_2O_7$ and $HNO_3-K_2Cr_2O_7$ we tried out the method described in the previous article [1], in which an electrode obtained by the decomposition of hydrogen peroxide on platinum is used for potentiometric titration.

In the absence of side reactions, titration of an acid solution of bichromate with alkali can be represented by the following reactions:

$$H_2SO_4 + 2KOH = K_2SO_4 + 2H_2O \quad (1)$$

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O. \quad (2)$$

In acid solution, however, bichromate reacts with hydrogen peroxide to form perchromates ($HCrO_6$) which are blue in color [2]. The per-compound formed is unstable and decomposes to form Cr_3 compounds.

The following reaction probably takes place:

$$K_2Cr_2O_7 + 5H_2O_2 + 4H_2SO_4 + 6KOH = 2Cr(OH)_3 + 4K_2SO_4 + 9H_2O + 4O_2. \quad (3)$$

When the reactions are written in this way it is clear that the amount of alkali used for reaction (3) is less than that required to neutralize one mol of $K_2Cr_2O_7$ and 4 mols of H_2SO_4 according to reactions (1) and (2).

Addition of hydrogen peroxide to the alkaline chromate solution leads to a color change from light yellow to brownish-red. In this case another per-compound of chromium is formed [2]:

$$2K_2CrO_4 + 2KOH + 7H_2O_2 = 2K_3CrO_8 + 8H_2O, \quad (4)$$

which is also unstable and decomposes as follows:

$$2K_3CrO_8 + H_2O = 2K_2CrO_4 + 2KOH + 3\frac{1}{2}O_2, \quad (5)$$

During this reaction the alkali used up in reaction (4) is completely regenerated.

In view of this it may be postulated that direct titration with alkali, of a solution containing bichromate and acid cannot give correct results. In fact, it was shown that on carrying out such an experiment considerable amounts of $Cr(OH)_3$ flocs could be observed in the solution.

On the other hand, titration with acid of an alkaline solution of chromate is possible; this was demonstrated in practice. In addition, it was found that it could be done with the usual accuracy of volumetric determinations.

To carry out a titration, a known amount of alkali is added to the test solution; the concentration of alkali added should be in a slight excess over that required for complete neutralization of acid and for conversion of $Cr_2O_7^{2-}$ to CrO_4^{2-} ions. It is only after addition of this alkali that 3-5 ml of 3% hydrogen peroxide is added.* A back titration with acid is then made.

The indicator electrode used is a smooth platinum plate or grid. The saturated calomel electrode is used as the reference electrode.

* The concentration of hydrogen peroxide in the test solution does not affect the value of the electrode potential. The amount of hydrogen peroxide added, however, should be sufficient to last out the whole of an analysis. In the given instance, the hydrogen peroxide concentration drops not only on account of its catalytic decomposition on platinum, but also as a result of reaction (4).

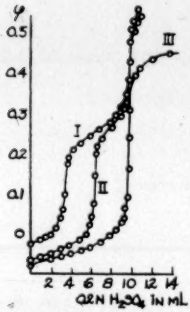


Fig. 1. Potentiometric titration curves for an alkaline solution chromate

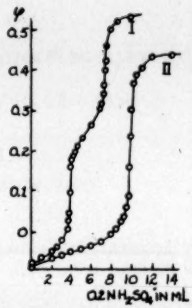


Fig. 2. Potentiometric determination of bichromate and strong acid after addition of alkali.

Solutions containing K_2CrO_7 and acid were prepared in order to check the method. The concentration of the original solution of bichromate was determined iodometrically.

Fig. 1 represents the titration curve for solutions of bichromate (0.631 (I) and 0.305 (II) mmol), not containing acid after addition of 1.970 mmol of KOH. For comparison, a curve for the potentiometric titration of the same amount of alkali is given (Curve III).

The first sloping part of the curve corresponds to neutralization of alkali according to reaction (1). The end of this process is accompanied by a well-defined potential jump. The second slope corresponds to the reaction.

$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O. \qquad (6)$$

The amount of acid necessary to form 1 g-ion of $Cr_2O_7^{2-}$ by reaction (6) is equivalent to the amount of alkali used in reaction (2). The position of the second potential jump, corresponding to complete change over of $Cr_2O_4^{2-}$ to $Cr_2O_7^{2-}$ coincides with the rise in the titration curve of the alkali.

In comparison with Curve III, the upper part of the titration curve for chromate is at much higher positive potential values. This fact is determined probably by the fact that the electrode used is at the same time an oxidation-reduction electrode and reacts in the presence of per-compounds of chromium in solution.

Titration of Mixtures of Potassium Bichromate-Sulfuric Acid and Potassium Bichromate-Nitric Acid.

Test	Amount taken, mmols			Amount found, mmols			Experimental error, in %		
No.	H_2SO_4	HNO_3	$K_2Cr_2O_7$	H_2SO_4	HNO_3	$K_2Cr_2O_7$	H_2SO_4	HNO_3	$K_2Cr_2O_7$
1	0.500	–	–	0.502	–	–	+0.4	–	–
2	1.000	–	–	1.000	–	–	±0.0	–	–
3	–	0.756	–	–	0.760	–	–	+0.6	–
4	–	1.071	–	–	1.072	–	–	+0.1	–
5	–	–	0.305	–	–	0.304	–	–	−0.3
6	–	–	0.631	–	–	0.630	–	–	−0.2
7	–	–	1.222	–	–	1.225	–	–	+0.2
8	0.500	–	0.617	0.500	–	0.626	±0.0	–	+1.5
9	0.300	–	1.519	0.300	–	1.515	±0.0	–	−0.3
10	–	0.756	0.815	–	0.758	0.820	–	+0.3	+0.6
11	–	0.756	0.916	–	0.764	0.920	–	+0.8	+0.5

When both bichromate and acid are present together in solution, the back titration curve after addition of alkali is of the same shape as Curves I and II in Fig. 1. However, in this case, as Fig. 2 shows, the position of the second jump on Curve II does not coincide with the sudden rise in Curve II. This difference is determined by the expenditure of alkali in neutralizing free acid in the test solution.

If the concentration of the alkali used is known, then on the basis of reactions (1) and (6), the content of $Cr_2O_7^{2-}$ and H^+ can be calculated according to the formulas:

$$a = \frac{1}{2}(V_2 - V_1) \cdot n \quad \text{and} \quad b = Vn' - V_2 n,$$

where a is the amount in g ions of $Cr_2O_7^{2-}$, b is the amount in g ions of H^+; V_1 and V_2 are the volumes of acid corresponding, respectively, to the first and second potential jumps on the titration curve; V is the volume of alkali added; n' is the normality of the alkali; n is the normality of the acid.

Results are given in the Table, which gives an idea of the accuracy of the method.

A basic source of error is the presence of sodium carbonate in the alkali. In such a case, that part of the curve which corresponds to titration of chromate is drawn out. The method described can be used for the analysis of chromates in alkaline solutions, and also for the determination of $Cr_2O_7^{2-}$ and CrO_4^{2-} when present together.

SUMMARY

1. A potentiometric method for the analysis of bichromate and strong acid when present together has been worked out. The method is based on a back titration with acid of test solution which has been made alkaline, using an electrode obtained by the catalytic decomposition of hydrogen peroxide on platinum.

2. It has been shown that in the presence of hydrogen peroxide, direct titration with alkali of acidified bichromate solutions leads to incorrect results.

Received October 26, 1953

LITERATURE CITED

[1] I. E. Flis, J. Anal. Chem., this issue, p. 38.*

[2] B. V. Nekrasov, "A Course of General Chemistry", State Chem. Press, 1952.

---

* See Consultants Bureau English Translation, p. 31.

BLANK
PAGE

FUNCTIONAL ANALYTICAL GROUPS FOR IRON AND BISMUTH

N. M. Turkevich

Lwov State Medical Institute

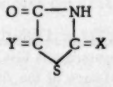
In our previous communications [1, 2], it was pointed out that ferric chloride can be used as a reagent to detect materials genetically related to thiazolidene derivatives, and also for their alkaline hydrolysis products. On the basis of these investigations, and on the reactions with bismuth salts given below, it is possible to establish functional analytical groups for iron and bismuth, which determine the appearance of characteristic colors and formation of sparingly soluble precipitates.

The table contains details of characteristic reactions with iron and bismuth salts. Negative, indefinite, or non-characteristic reactions are denoted by a (−), while deviations from the typical reaction, as a result of the presence of acetyl, weighting (i.e., groups which make the molecule heavier), or auxochromic groups are remarked upon separately in the text.

Functional Analytical Groups for Trivalent Iron

The group $-\underset{\underset{H}{|}}{N}-\overset{\overset{N\cdot OH}{\|}}{C}-$ which is found in molecules of 2'-hydroxypseudothiohydantoins (see the formula given below X = N·OH) [3], is a functional-analytical group for Fe^{III} which gives rise to lilac colors. Substitution of the hydrogen atom in the group indicated by an alkyl group leads to loss of specificity, as a result of which 3-methyl-2'-hydroxypseudothiohydantoin does not give a characteristic reaction, while the simple −2'-hydroxypseudothiohydantoin, and also its 5-methyl- and 5-benzylidene derivatives give a lilac color with Fe^{III}. Apparently, the complex compounds which are formed contain a five-membered ring with iron as the hetero atom in their molecules.

A functional-analytical group for Fe^{III} which gives rise to a blue color in ammoniacal media is the $-\overset{\overset{O}{\|}}{C}-\overset{\overset{SH}{|}}{C}=$ group, which is found in the molecules of mercaptocarboxylic acids; these are easily formed during alkaline hydrolysis of thiazolidene derivatives of the general formula



The substituent "Y" acts as an auxochrome, and it is not only aromatic, but also alicyclic substituents with several double bonds which can deepen the color by forming iron-ammine complex compounds with a green or yellowish green color.

Thioglycollic acid and its methyl-, isopropylidene-, cyclopentylidene-, and cyclohexylidene-derivatives all give blue or violet colors with Fe^{III}. Fe^{III} gives blue-green or green colored compounds with the benzylidene-, methylbenzylidene-, phenylbenzylidene-, p-dimethylaminobenzylidene-, 5-oxo-4-carbethoxy-3-phenyl-1-methylhexylidene-, allylisopropylidene-, and citrylidene-derivatives of thioglycollic acid.

The naphthylamide of thioglycollic acid, which contains the functional group mentioned above in its molecule, forms a white precipitate with Fe^{III} in ammoniacal solution, while the solution is colored violet.

A functional analytical group for Fe^{III}, which gives rise to the formation of a red color in neutral and weakly acid media, is the thioamide group in its tautomeric form $-\overset{\overset{SH}{|}}{C}=N-$. Since they contain this group in their molecules, thiourea and thiocyanic acid, which may be regarded in its tautomeric form as the simple thioamide CS=NH, give characteristic reactions with Fe^{III}. It should be noted that HSCN is a very sensitive reagent, while thourea only gives a positive reaction at very high concentrations. This is connected, no doubt, with the partial tautomeric conversion of thiourea into isothiourea containing a free mercapto group.

TABLE

Reagents	$FeCl_3$ in neutral and acid media	$FeCl_3$ in ammoniacal medium	$BiCl_3$ in weakly acid medium
Rhodanines X=S	–	–	–
Pseudothiohydantoins X = NH	–	–	White precipitates
2'-hydroxypseudothiohydantoins, not substituted on the nitrogen atom, X = N·OH	Lilac color	Lilac color	–
Thiazolidones-4, substituted on the nitrogen atom	–	–	–
Thiourea	Reddish-brown color	Colorless solution	Yellow color
Thiazolidenediones, X = O	–	–	–
α-Mercaptocarboxylic acids	–	Blue color	–
Thiocyanic acid and its salts	Blood-red color	Colorless solution	Yellow color
Carbaminylthioglycolamides	–	–	–
Dithioglycolamides	–	–	–

Acylation of the thioamide group leads to loss of its specificity, as a result of which compounds containing the group $-CS-\underset{|}{N}-CO\cdot R$, do not serve as reagents for Fe^{III}; rhodamines belong to this type of compound (we tried 28 different rhodamines), and also thiobarbituric acids, (e.g., thiopental), acetylthiourea, methylthiouracil, et. al.

Functional-Analytical Groups for Bismuth

The thioamide group is a functional-analytical group for bismuth, with which it gives rise to a yellow compound. Compounds which contain this group and which are reagents for bismuth are: thiourea [4], thiocyanic acid and its water soluble salts, and also many derivatives of thiodiazolidene, and triazolidene, etc., tested by Dubsky and coworkers [5].

It should be noted that it is only that thioamide group which is capable of tautomeric conversion to the mercapto group:

$$-\underset{\underset{S}{\|}}{C}-NH- \rightleftharpoons -\underset{\underset{SH}{|}}{C}=N-$$

that possesses functional-analytical properties, as in the case with Fe^{III}:

Substitution of the hydrogen atom by alkyl or aryl substituents leads to loss of this specificity on the part of the thioamide group, as a consequence of which, mustard oils RNCS (in the same way as esters of thiocyanic acid RSCN) do not give characteristic reactions for Bi. Acylation of the thioamide group also deprives it of its specificity, since the electron displacement which is caused by the carbonyl group hinders tautomerism $R\cdot\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-C-$, i.e., hinders the formation of a mercapto group.

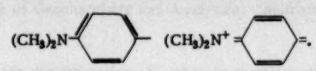
Some groups, connected with the thioamide group, deepen the color of the bismuth compounds formed, as a result of which these compounds acquire orange or red colors. Such groups are: the methyl (in thiocetamide [6]) and aminthiazolyl (in chryseine) groups. The color also deepens appreciably, particularly when there are two thioamide groups present in the molecule, as in the so-called bismuthiols [7, 8].

The non-acylated amine group $-N=$ is a functional-analytical group for bismuth, with which it leads to the formation of sparingly soluble precipitates. The reaction products in this case belong to various types according to the nature of the medium used. In non-aqueous media (alcohol, acetone, ether, ethyl acetate, etc.), substituted ammines form. Precipitates are also formed in the presence of free acid, but they belong to the class of complex salts in which the bismuth atom is in the anion; e.g., by the action of quinoline on a hydrochloric acid solution of bismuth chloride, it is not the amine that is formed, but its conversion product – a chloro bismuthate of the composition $[C_9H_7NH_2][BiCl_5]$ [9].

We found that the ammine compounds of bismuth which are stable to hydrolysis may also be formed in aqueous media. For example, we managed to make in this way a non-substituted ammine $C_6H_5O_7Bi\cdot NH_3$ [10] and the phenylammine $C_6H_5O_7Bi\cdot NH_2C_6H_5$ of bismuth citrate.

A number of bismuth ammines are described in the literature which were obtained from aniline [11], pyridine, quinoline, naphthylamine [9], and from other aromatic and heterocyclic amines. We found that thiazolidene derivatives, whose molecules contain non-acylated amine groups, also precipitate bismuth as substituted ammines (aminates). We prepared compounds of bismuth chloride with p-dimethylaminobenzylidenerhodamine, pseudothiohydantoin, 5-benzylidene-3-allyl-pseudothiohydantoin, and p-dimethylaminobenzylidene-3-allylpseudothiohydantoin.

p-Dimethylaminobenzylidenerhodamine is an intramolecular ionoid dye [12] with a dark red color, which is a result of the displacement of the electrons to the ring and the possibility of the formation of a quinoid group:



On pouring solutions of this reagent and bismuth chloride together into anhydrous acetic acid, a crystalline ammine is formed whose composition corresponds to $3BiCl_3 \cdot 2(CH_3)_2N \cdot C_6H_4 \cdot CH = C_3HONS_2$, and whose color is yellow, just like the rhodamines without the auxochromic groups. This is a result of the fact that the ammine contains a bond between the nitrogen and bismuth atoms $Cl_3Bi^- -N^+(CH_3)_2$, which hinders intramolecular ionoid regrouping. When water, as such, or even moisture causes the ammine to hydrolyze, this bond is broken and the material acquires a red color.

Analysis of preparation. 30.2 mg substance: 1.00 ml N_2 (749 mm, 23°)
115.8 mg substance: 60.5 mg Bi_2S_3
97.0 mg substance: 6.0 ml 0.1 N $AgNO_3$

Found %: N 3.76; Bi 42.47; Cl 21.93
$C_{24}H_{24}O_2N_6S_4Cl_9Bi_3$. Calculated %: N 3.80; Bi 42.51; Cl 21.64

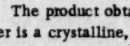
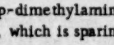
A similar compound, which is obtained on pouring pseudothiohydantoin and bismuth chloride into anhydrous acetic acid, has the composition $BiCl_3 \cdot C_3H_3ONS = NH$. It is a white, crystalline compound, which is insoluble in water and organic solvents.

The compound formed between bismuth chloride and 5-benzylidene-3-allylpseudothioydantoin, which is formed in a similar manner, has the composition $BiCl_3 \cdot C_6H_5 \cdot CH = C_3ONS(C_3H_5) = NH$ and is a white material, which is only very sparingly soluble in mineral acids.

The product obtained by pouring $BiCl_3$ and 5-(p-dimethylaminobenzylidene)-3-allylpseudothiohydantoin together is a crystalline, strongly hygroscopic material, which is sparingly soluble in alcohol and acetic acid.

SUMMARY

1. The thioamide group is a functional-analytical group for Bi (yellow colors) and Fe^{III} (red or reddish-brown colors); its specificity is determined by its capacity to tautomerize. The functional-analytical properties of the thioamide groups disappears on acylation.

2. The groups  (lilac colors) and  (blue colors) are functional-analytical groups for Fe^{III}.

3. The non-acylated amine group $-N=$ is a functional-analytical group for Bi, which gives rise, in non-aqueout media (alcohol, acetone, ether, etc.) to the formation of sparingly soluble ammines.

Received May 10, 1952

LITERATURE CITED

[1] N. M. Turkevich, M. P. Makukha, Ukrainian Chem. J., 16, 648 (1950).
[2] N. M. Turkevich, M. P. Makukha, J. Anal. Chem., 6, 308 (1951).
[3] N. M. Turkevich, O. P. Melnichuk, Ukrainian Chem. J., 16, 459 (1950).
[4] R. Petit, R. Meraux, Chim. et Ind., 43, 629 (1940).
[5] J. Dubsky, A. Okač, J. Trtilek, Mikrochemie, 17, 322 (1935).
[6] N. V. Vavilov, J. Appl. Chem., 11, 356 (1938).
[7] J. Dubsky, A. Okač, J. Trtilek, Z. anal. Chem., 100, 408 (1935).
[8] L. M. Kulberg, "Organic Reagents in Analytical Chemistry", Moscow-Leningrad (1950).
[9] O. Hauser, L. Vanino, Ber., 33, 2272 (1900); 34, 417 (1901).
[10] N. M. Turkevich, Ukrainian Chem. J., 15, 243 (1949).
[11] H. Schiff, Ber., 34, 804 (1901).
[12] S. A. Voznesensky, "Inner Complex Compounds and Their Application in Analytical Chemistry", Moscow-Leningrad, 1938.

BLANK
PAGE

MICRO DETERMINATION OF CARBON IN METALS

P. A. Kryukov and E. V. Rengarten

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR, Moscow

The normal methods used for the determination of carbon in metals require ca. 1-2 g of sample when the carbon content is very small. In many cases it is out of the question to get such large amounts of sample, e.g., during a study of the surface layers of metals, or of experimental alloys on a laboratory scale, particularly, in the case of rare, and new metals and alloys.

During a study of samples of metallic titanium obtained from expefimental melts, we were confronted with the problem of determining extremely small amounts of carbon, of the order of thousandths of a per-cent on small samples.

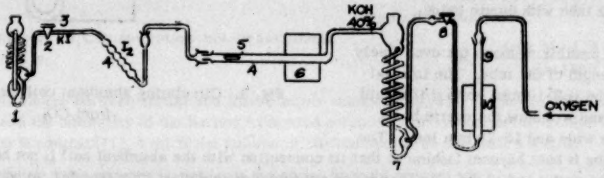


Fig. 1. Schematic diagram of the set-up.

The method in general use for the determination of carbon from the volume of CO_2 evolved is inapplicable in practice to such small amounts.

We tried to use the principle of a method suggested by Bruns, et. al. [1], for the determination of small amounts of carbon; this method consists of a continuous analysis of the gas mixture based on measurement of the electrical conductivity of a $Ba(OH)_2$ solution, which is used as absorbent. This principle has been used by several authors, [2, 3, 4], for the macroanalysis of metals.

In order to adapt this method for microanalysis, we had to introduce a number of essential changes; after testing many variants, we eventually decided on the set-up shown in Fig. 1.

1. The oxygen which is to be used for the combustion of the test sample is passed from the gasometer into a quartz tube filled with cupric oxide heated by an electric oven to 600-700°. This is an essential precaution to ensure combustion of small amounts of CO, hydrocarbons, and most important, vapors of organic materials evolved by the grease, rubber connections, etc.. The copper oxide column should be at least 10 cm long and 15-20 mm in diameter. The tube is fixed vertically, since in a horizontal position channeling of the cupric oxide may easily occur, thus leading to a loss of efficiency (Fig. 2). The temperature of the tube containing cupric oxide must be controlled by means of a thermocouple and a galvanometer, since at temperatures above 700°, the cupric oxide begins to clinker and to react with the quartz.

The top inlet end of the tube, which is fitted with a ground glass joint should project at least 10-15 cm from the oven so that the joint is not heated. The lower, outlet end of the tube which is bent to the shape of a right angle should also stick out about 10 cm from the side of the oven (see Fig. 2).

2. Purification of oxygen from traces of CO_2 was ensured by using a circulating spiral absorbent tube (Fig. 3), containing ca. 40 ml of 40% KOH. It is of vital importance that the connections between the outlet of the tube containing cupric oxide and the tap, and between the tap and the inlet tube of the absorbent coil should abut on each other.

3. The quartz combustion tube is 2.2-2.5 times as long as the oven used, i.e., 25-30 cm for an oven length of 10-11 cm. The internal diameter of the oven should be 10 mm gerater than the external diameter of the combustion tube, so that it is possible to insert the end of a thermocouple fixed to the oven, freely between them.

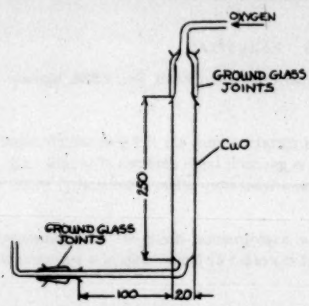


Fig. 2. The quartz tube with cupric oxide.

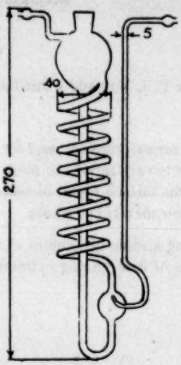


Fig. 3. Circulating absorbent coil for cleaning the gas from CO_2.

It should be possible to move the oven freely along the whole length of the tube. The internal diameter of the tube is 9-10 mm, so that it should be easy to insert and withdraw the quartz boats which are 5-6 mm wide and 15-20 mm long. The inlet end of the tube is bent bayonet fashion so that its connection with the absorbent coil is not heated by radiation from the oven. The outlet end of the tube is widened out into a ground glass joint (see Fig. 4) which is fitted with a ground-glass cap. This joint should be lubricated with the smallest possible amount of good quality vacuum grease.

4. In order to control the oxygen flow accurately during combustion, a tap is used (2, Fig. 1), which has a long handle and two grooves on its shaft. These grooves, of length 0.25 of the circumference made with a fine file or needle file, gradually come together from opposite sides of the shaft. This tap is also smeared with the minimal amount of vacuum grease or beeswax.

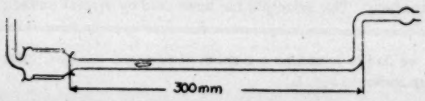


Fig. 4. Quartz combustion tube + boat.

The volume of the outlet tube of this tap and the inlet tube of the absorbent coil up to the narrow nozzle should be a minimum (0.3-0.5 ml); otherwise, it will be difficult to ensure that the bubbles pass at a regular rate into the coil. The tap is firmly and securely mounted on the thermostat cover.

5. The small absorbent coil (Fig. 5), which contains 4 ml of a weak solution of $Ba(OH)_2$ (0.01-0.002 N), is widened out at its lower end, where two electrodes of platinum black are fused in. Movement of gas bubbles along the coil at the same time give rise to a continuous circulation of solution. The upper, outlet part of the coil is covered with a soda lime tube as protection from CO_2. For preliminary regulation of this apparatus, it is useful to connect a small rheometer to the outlet of this tube, to ensure a gas rate of ca. 10-15 ml/minute (this rheometer is not shown in the schematic diagram). The absorbent coil is immersed up to half of the top bulb in a water thermostat (Type TS-15), which maintains the temperature at $25 \pm 0.1°$.

6. When the test material contains sulfur, then it is necessary to introduce a spherical absorbent tube containing 0.01 N iodine solution in front of the absorbent coil, between the tap and the combustion tube, in order to trap sulfur compounds; this tube is followed by a second tube containing solid potassium iodide, to trap iodine vapor (Fig. 6).

A photograph of the set-up used is shown in Fig. 7 [see plate, page 65].

7. An ordinary Wheatstone bridge arrangement is used for measuring the electrical conductivity of the barium hydroxide solution; the two arms of the bridge are composed of standard resistances and a resistance box,* while the other two arms comprise a Kohlrausch bridge (rheocord on a drum). AZG-2 sound wave generator is used for supplying

* (10 - 1000 Ω).

the bridge with a high frequency current of 800-10,000 cycles. An electronic oscillograph type EO-4 or EO-5 across the diagonal was used as the null instrument (Fig. 7 [see plate, page 65]—general view of the set-up). In connecting the apparatus it is necessary to use a thick-multi-core wire between resistance box and measuring cell (coil) so that the resistance can be regarded as negligible. The method of determining the electrical conductivity has been described in more detail in another article [5].

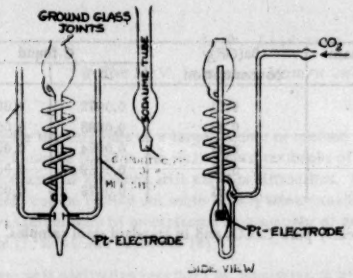


Fig. 5. Circulating coil for CO_2 absorption and measurement of electro-conductivity.

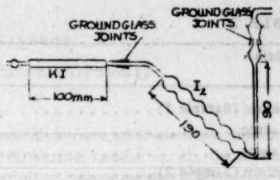


Fig. 6. Bulb tube with I_2 solution for trapping sulfur compound.

The percentage of carbon is calculated according to the equation

$$\%C = \frac{\Delta n \; 4.31 \cdot 4 \cdot 6 \cdot 100}{m \cdot 1000},$$

where Δn is the difference between initial and final electro-conductivity; 4.31 is the ratio between the specific electro-conductivity and the normality of the barium hydroxide solution. For low barium hydroxide concentrations, 0.01-0.002 N, this value is constant [1]; 4 ml is the volume of barium hydroxide solution; $6 = C/2$.

After substituting these numerical quotients the above formula reduces to:

$$\%C = \frac{\Delta n \cdot 10.3}{m},$$

where Δn is the difference between initial and final electro-conductivity; m is the weight of sample in g.

A determination is carried out as follows: boat and sample are placed in the left hand side of the combustion tube, but not too near the ground-glass joint (see schematic set-up); oven 10 plus CuO is then connected to it. The combustion oven 6 is moved to the right, up to the end and switched on. All the apparatus is connected up and oxygen passed through at a rate of 10-15 ml/minute. The apparatus is tested to ensure that it is hermetically sealed. The gas rate is regulated by means of a tap 2 (see set-up). After the apparatus has been swept for 20 minutes with the temperature of the oven used for heating the CuO at 600-700°, the absorbent coil is disconnected (without stopping the gas flow) and filled with 4 ml of $Ba(OH)_2$ solution (0.01 or 0.002 N).

TABLE 1

Material	Weight of sample, in g	$Ba(OH)_2$ concentration	C content, %	C found		Absolute error, in %
				in %	in g	
$CaCO_3$	0.000813	0.01	12	13.2	0.000107	+1.2
The same	0.001283	0.01	12	12.9	0.000166	+0.9
Steel	0.0172	0.002	0.074	0.069	0.000011	−0.005
The same	0.0192	0.002	0.074	0.071	0.000013	−0.003
"	0.0236	0.01	0.47	0.49	0.000114	+0.02
"	0.0144	0.01	0.47	0.52	0.000074	+0.05

The coil is filled with barium hydroxide from a microburet with a long, fine, drawn out tip. The end of the buret should be fixed during filling with $Ba(OH)_2$ so that its tip is in the lower, widened out part of the coil. Unless this precaution is observed, an air bubble may form which is will be difficult to get rid of. When the coil has been filled, it is connected up again to the apparatus and the initial value of the electro-conductivity of the solution determined while oxygen is still being passed through. The conductivity is measured a few times at intervals of 3-5 minutes, until the value registered on the bridge is constant for 10 minutes.

When a constant reading has been reached on the bridge, oven 6 (see diagram) is moved on to the boat.* After 0.5-1 minute according to the amount of test sample, ignition starts, and after 1-2 minutes, the oscillograph begins to register changes in the concentration of the $Ba(OH)_2$ solution. Readings are made on the Kohlrausch bridge when the sinusoidal curve on the oscillograph screen becomes a straight line; this corresponds to minimum current through the diagonal. Evolution of carbon dioxide and its subsequent absorption is considered complete when the readings of the bridge are constant for at least 10 minutes.

TABLE 2

Material	Weight of sample, in g	$Ba(OH)_2$ concentration	C found	
			in %	in g
Titanium (Sample 1)	0.2168	0.01	0.0072	0.0000157
The same	0.1122	0.01	0.0088	0.0000108
The same	0.1445	0.01	0.0084	0.0000121
Titanium (Sample 2)	0.1165	0.01	0.0069	0.00000804
The same	0.1062	0.01	0.0079	0.00000838

Using this method, we determined carbon in chemically pure $CaCO_3$ and in standard steel samples. Results of such determinations are adduced in Table 1.

These results show that carbon can be determined in gamma amounts on small samples with an accuracy of 1 to 0.01% absolute.

Results of the analysis of two samples of metallic titanium are given in Table 2.

The smallest amount of carbon which we determined in a test sample was 8 γ.

SUMMARY

A micro method has been worked out for the determination of carbon in metals whereby gamma amounts of carbon can be determined on small samples.

Received November 3, 1954

LITERATURE CITED

[1] B. Bruns, G. Braude, and D. Tsiklis, J. Anal. Chem., 2, 5 (1947).

[2] R. M. Focobr, E. L. Bennet, Y. H. Harley, Anal. Chem., 22, No. 3 (1950).

[3] "Titanium – The Light Metal," Light Metals, No. 178, 9-13, 1953.

[4] J. E. Still, L. A. Duncey, R. C. Chirnside, Analyst, No. 934, p. 4, 1954.

[5] A. P. Kryukov, "Hydrochemical Materials", Vol. XXII, 1954.

* The oven used for combustion of the test sample should be kept at 900° all the time.

PRECIPITATION OF QUADRIVALENT VANADIUM WITH 5,7-DIBROMO- AND 5,7-DIIODO-8-HYDROXYQUINOLINE

I. P. Alimarin and V. G. Kryukov

The M. V. Lomonosov Moscow Institute of Fine Chemical Technology

Despite the existence of a large number of method for separating vanadium from other elements, information about which can be found in the well-known textbooks of A. M. Dymov, Hillebrand, Lendel, et. al., the separation of small amounts of vanadium still presents difficulties. Separation of vanadium from a number of elements, including iron, can be carried out more readily when vanadium is present in solution in the fourth valency state. Quadrivalent vanadium may be precipitated by a number of precipitants, including ammonium benzoate, ammonium cinnamate [1, 2, 3], and cupferron [4].

Some new qualitative reactions for precipitation of quadrivalent vanadium were described recently in an article by Kuznetsov and Kozyreva [5].

According to our observations, quadrivalent vanadium is quantitatively precipitated by 8-hydroxyquinoline. Nevertheless, it is not always convenient to use this reagent, since the pH required for precipitation of vanadium is fairly high.

Of greater interest as reagents, as compared with 8-hydroxyquinoline, are the dihalo substituted derivatives. It is well-known, for example, that 5,7-dichloro- or 5,7-dibromo-8-hydroxyquinoline precipitate elements from more acid solutions than unsubstituted 8-hydroxyquinoline [6-9].

In this work, the precipitation of the vanadyl ion by 5,7-dibromo-and 5-7-diiodo-8-hydroxyquinoline is described.

5,7-Dibromo-8-hydroxyquinoline has already been in use as an analytical reagent for some time. Thus, Berg [6-9], and Zanko and Barsuk [10, 11], used this reagent for the quantitative determination of Cu, Fe, Ti, and Al; Gutzeit and Monnier [12], recommend it as a qualitative reagent for trivalent vanadium; recently, Bartelmus and Hecht [13], used it for the precipitation of germanium-molybdenum heteropolyacids. We were the first to recommend the use of the 5,7-diiodo-8-hydroxyquinoline for the determination of vanadium; we could find no reference to the use of this reagent in the literature.

The 5,7-dibromo-8-hydroxyquinoline reagent used in our work was synthesized by the Berg and Kustenmacher method [8], while the corresponding diiodo derivative was prepared by Zeifman's method [14], by iodination of 8-hydroxyquinoline in alcoholic solution.

We studied the stability of solutions of vanadium (IV) to oxidation by atmospheric oxygen at various pH's, and showed that it is better to precipitate V (IV) by means of the dihalo derivatives of 8-hydroxyquinoline, than with unsubstituted 8-hydroxyquinoline.

Stability of Vanadyl Solutions to Oxidation by Atmospheric Oxygen at Various pH's.

According to Syrkomsky and Klimenko [15], acid solutions of vanadyl salts are completely stable even at the boiling point.

Our experiments in evaluating the stability of vanadyl sulfate solutions to atmospheric oxygen were first carried out in a solution with a pH of 1.8, exposed to daylight. 10 ml lots of a $VOSO_4$ solution containing 2.34 mg vanadium/ml were left in open beakers for a few days. After varying time intervals the amount of vanadium (IV) left was determined by titration with 0.1 N $KMnO_4$. It was found that the vanadium (IV) concentration did not change appreciably after standing for 20 days.

In another series of tests, air was blown through the $VOSO_4$ solutions of varying pH values. The results obtained, which characterize the stability of vanadyl solutions to oxidation are adduced in Table 1.

Solutions of vanadyl salts with a pH of 2 are completely stable to atmospheric oxygen and to ultra-violet radiation. After 15 hours irradiation of vanadyl solutions by a PRK-4 mercury lamp at a distance of 8 cm from an open quartz beaker containing vanadyl sulfate solution, no decrease in vanadium (IV) concentration could be detected.

TABLE 1

Stability of Vanadyl Sulfate Solutions to Atmospheric Oxygen

Time for which air is passed through the solution (in hrs)	pH	0.1 N $KMnO_4$ (in ml)
0	1.8-2	14.08
8	1.8-2	14.08
20	1.8-2	14.05
60	1.8-2	14.05
160	1.8-2	14.00
300	1.8-2	14.00
0	3	14.30
50	3	14.15
0	4	14.30
60	4	14.20

Volume of $VOSO_4$ 10 ml, concentration of V 2.34 mg/ml

Solutions of vanadyl salts with pH > 4 are less stable to atmospheric oxidation. On standing, the blue color gradually changes to a dirty green, or a dark precipitate is formed. The stability is less, the greater the pH.

The high stability of sulfuric acid solutions of vanadyl salts to air means that for their preparation by reduction of vanadium with SO_2, even pure air can be blown through the solution to remove excess SO_2, as well as CO_2 which is generally used.

The Behavior of 5,7-Dibromo- and 5,7-Diiodo-8-hydroxyquinoline with Various Elements

5,7-Dibromo- and 5,7-diiodo-8-hydroxyquinoline precipitate many elements at various pH values. In acid and in weakly acid solution of pH up to 4, these reagents precipitate the following elements: Sb^{III}, Cd, Cu^{II}, Bi, Hg_2^{II}, Hg^{II}, Pb, which form yellow precipitates of varying shades. Fe^{II}, and Fe^{III} give black precipitates, while Cr^{III} gives a dirty blue or blue-black precipitate.

At high pH values, Al, Zn, Co, Ni, Mn, V^{IV} are precipitated with the formation of yellow precipitates of varying shades, while V^{V} forms a greenish black precipitate.

Precipitation of the Vanadyl Ion with 5,7-Dibromo- and 5,7-Diiodo-8-hydroxyquinoline

On addition of an acetone solution of 5,7-dibromo- or 5,7-diiodo-8-hydroxyquinoline to quadrivalent vanadium solutions with a pH of 4-5, yellow precipitates are formed.

After drying the vanadyl 5,7-dibromo-8-hydroxyquinolate at 150-200°, the precipitate has the composition $VO(C_9H_4ONBr_2)_2$.

Calculated for $VO(C_9H_4ONBr_2)_2$: C 32.2%; V 7.6%
Found %: C 32.5; 32.6; 32.8; V 7.8; 7.6; 7.5

The precipitate of vanadyl 5,7-diiodo-8-hydroxyquinolate on drying at 170-185° has the composition $VO(C_9H_4ONI_2)_2$.

Calculated for $VO(C_9H_4ONI_2)_2$: V 5.9%
Found %: V 6.0; 5.9; 6.1

These compounds do not change outwardly and do not lose weight on drying at temperatures up to 200° (dibromo-derivative) and up to 180° (diiodo-derivative).

These products on drying at room temperature or in a drying oven under the above conditions of temperature, are yellow with a light greenish shade (diiodo-derivative).

These complex compounds are insoluble in water and in acids of normality up to 0.6 N, they dissolve in concentrated acids, however; alkalis do not produce any apparent change. The complexes are insoluble in carbon tetrach oride and in ethyl ether; they are soluble in acetone, methyl-, ethyl-, and isoamyl alcohols, benzene, toluene, xylene, amyl acetate, and chloroform to give solutions with colors varying from a light to a dark brown or dark red. They are particularly soluble in chloroform and amyl acetate.

Their behavior with benzene and toluene is of interest; the dibromo-derivative dissolves readily in xylene but less readily in benzene, the diiodo derivative, however, is more soluble in benzene than in xylene.

As tests showed, complete precipitation of quadrivalent vanadium is achieved on addition of an acetone solution of the reagent to solutions of vanadyl salts with a pH of 4. There is no precipitation at all from more acid solutions.

The completeness with which vanadium (IV) is precipitated from solutions with pH = 5 is illustrated by the results given in Tables 2 and 3. All the precipitates were weighed after drying in an oven at 150-200° (dibromo-derivative) or at 170-180° (diiodo-derivative).

TABLE 2

Determination of Vanadium (IV) as Vanadyl 5,7-Dibromo- and 5,7-Diiodo-8-hydroxyquinolates

V taken (in mg)	$VO(C_9H_4ONBr_2)_2$ formed (in mg)	V found [calculated as(V)](in mg)	Difference (in mg)
11.70	153.8	11.69	−0.01
11.70	154.2	11.72	+0.02
11.70	154.0	11.70	0.00
11.70	153.0	11.65	−0.05
11.70	154.0	11.70	0.00
	$VO(C_9H_4ONI_2)_2$ (in mg)		
12.25	206.9	12.28	+0.03
12.25	207.0	12.29	+0.04
12.25	206.3	12.25	0.00
12.25	205.7	12.21	−0.04
4.96	83.4	4.95	−0.01
4.96	83.9	4.98	+0.02
4.96	83.2	4.94	−0.02
4.96	83.3	4.95	−0.01

TABLE 3

Determination of Vanadium as V_2O_5 after Calcining Precipitates of the Vanadyl Hydroxyquinolates

Vanadium taken (mg)	Vanadium found (mg)	Difference (mg)	Observations
11.88	11.87	−0.01	Dibromo-8-hydroxyquinolate
11.54	11.48	−0.06	
11.36	11.14	−0.22	
11.48	11.20	−0.28	
12.25	12.49	+0.24	Diiodo-8-hydroxyquinolate
12.28	12.15	−0.13	
12.05	12.32	+0.27	
4.53	4.70	+0.17	
4.88	5.10	+0.22	

In order to check that the formulas attributed to these compounds are correct and that the factors used for converting them to vanadium are also true, all the precipitates, after weighing as the quinolates, were calcined in porcelain crucibles and weighed as V_2O_5 (Table 3).

To convert the 5,7-dibromo-hydroxyquinolate to vanadium, the factor is 0.0760.

Since complete precipitation of vanadium is possible by the use of these reagents, they are recommended as precipitants of quadrivalent vanadium.

Methods for their use are described below.

Recommended Method for the Precipitation of Quadrivalent Vanadium with 5,7-Dibromo-8-hydroxyquinolate

A few drops of methyl orange are added to 150-200 ml of a vanadyl sulfate solution containing 5-12 mg of vanadium, whose acidity is not greater than 0.05-0.1 N, a solution of sodium acetate is then added, also dropwise, until the solution acquires a yellowish-orange color which corresponds to a pH of ca. 4. The solution is heated on a water bath to 50-55°. A saturated (ca. 1%) solution of 5,7-dibromo-8-hydroxyquinoline is then added in small portions with careful mixing until precipitation is complete. A bulky precipitate with a yellow color is formed. That excess reagent has been added can be easily checked by the appearance of white flocs of reagent. After heating for 15-20 minutes on the water bath, the precipitate is filtered through a No. 4 crucible.

The filtered precipitate is washed with 100 ml of wash liquor (10 ml acetone, 10 ml 1 N HCl and 80 ml water) and then with hot water. After drying at 150-200° the precipitate is weighed as $VO(C_9H_4ONBr_2)_2$. To convert to vanadium, the factor used is 0.0760.

Recommended Method for the Precipitation of Quadrivalent Vanadium with 5,7-Diiodo-8-hydroxyquinolate

The procedure employed in this case is identical with that given above for the dibromo reagent. The product in this instance, which is dried at 170-180°, corresponds to the formula $VO(C_9H_4ONI_2)_2$. The conversion factor is 0.0594.

SUMMARY

1. Conditions for precipitating vanadium (IV) by means of 5,7-dibromo- and 5,7-diiodo-8-hydroxyquinoline, respectively, are described; the properties of the compounds formed are also described.

2. Both reagents precipitate the vanadyl ion quantitatively from solutions with a pH of ca. 5. The yellow compounds which are formed, on drying at 150-200° (dibromo-derivative) or 170-180° (diiodo-derivative) correspond to the compositions: $VO(C_9H_4ONHa_2)_2$. These formulas are gravimetric formulas

The precipitates are soluble in concentrated acids, but are insoluble in alkalis. They dissolve readily in chloroform, amyl acetate, and xylene.

Received April 12, 1954

LITERATURE CITED

[1] F. M. Shemyakin, Factory Labs., 3, 986 (1934).

[2] F. M. Shemyakin, V. V. Adamovich, and N. P. Pavlova, Factory Labs., 5, 1129 (1936).

[3] F. M. Shemyakin and V. F. Chapygin, J. Appl. Chem., 8, 536 (1935).

[4] N. Furman, W. Mason, J. Pecola, Anal. Chem., 21, 1326 (1949).

[5] V. L. Kuznetsov and L. S. Kozyreva, J. Anal. Chem., 8, 90 (1953).*

[6] R. Berg, Z. anal. Chem., 70, 341 (1927).

[7] R. Berg. Z. anorg. Chem., 204, 208 (1932).

[8] R. Berg. H. Küstenmacher, Z. anorg. Chem., 204, 215 (1932).

[9] R. Berg, "The Application of o-Hydroxyquinoline in Analytical Chemistry", State Sci. Tech. Press, Moscow, 1937.

[10] A. M. Zanko, A. Ya. Barsuk, Factory Labs., 6, 675 (1937).

[11] A. M. Zanko and A. Ya. Barsuk, J. Appl. Chem., 9, 895 (1936).

[12] G. Gutzeit, R. Monnier, Helv, Chim. Acta, 18, 233 (1933).

[13] G. Bartelmus, F. Hecht Mikroch. Acta, 1954, 148.

[14] V. Zeifman, Proc. Inst. Pure Chem. Reagents, 16 80 (1939).

[15] V. S. Syrokomsky and Yu. V. Klimenko, "Vanadometry", Metallurgy Press, 1950.

* See Consultants Bureau Translation, page 101.

DIPHENYLCARBAZONE AS A REAGENT FOR THE COLORIMETRIC DETERMINATION OF GERMANIUM

G. S. Desmuk

Chemical Laboratory, University, Benares (India)

The formation of a yellow germanium-molybdenum complex [1] is used for the colorimetric determination of small amounts of germanium. The colored solutions of the complex formed for low germanium concentrations (< 40 mg/liter) follow Beer's law [2]; the reaction sensitivity is enhanced by reduction of the molybdenum in the complex to molybdenum blue [3-6]. We observed that addition of a drop of a saturated alcoholic solution of diphenylcarbazone to the yellow germanium-molybdate gives a purple color, similar to that which is developed in the well-known reaction of this reagent with Hg^{2+} [7]. Diphenylcarbazone also gives a rose or red color to aqueous solutions of ammonium molybdate (Feigl [8]). This color, just as the color obtained with Hg^{2+}, is destroyed on acidification of the solution with concentrated hydrochloric or sulfuric acids. In the case of germanium-molybdate, however, the purple color becomes blue, and this color is stable even in the presence of a large excess of acid. Acidification of ammonium molybdate, with excess acid before addition of an aqueous solution of GeO_2, or the use of a neutralized solution of sodium germanate do not lead to the formation of the characteristic blue color. It is known that the yellow color of germanium-molybdate is similar to the color of the phospho- and arseno-molybdates, but they are formed at comparatively higher hydrogen ion concentrations. Parallel experiments with phosphates and arsenates showed that the colorimetric reaction described above does not respond to these ions; their presence, however, lowers the reaction sensitivity, and at high concentrations of these ions, the blue color becomes pale and disappears almost completely.

Fluorides, tartrates, colored ions, and oxidizing and reducing ions should be removed before carrying out this reaction.

Although the blue color develops on addition of either hydrochloric acid or sulfuric acid, the color is more constant in the latter case. With hydrochloric acid the color develops immediately, but gradually disappears on standing for a long time. The color, may, however, be stabilized by heating the solution to the boiling point after addition of acid, or by protecting it from the action of direct sunlight.

Determination of the limits of sensitivity and concentration showed that the presence of germanium in such small amounts as 0.1 γ in 0.03 ml can easily be detected using the reaction described above.

Preliminary tests showed that the intensity of the blue color depends on the germanium concentration. These observations indicate a possible application of this reaction for the quantitative determination of germanium. Further work is being carried out along these lines.

The author wishes to express his thanks to Prof. Djoshi for his kind attention, and also to the National Institute of India for its cooperation.

Received August 18, 1954

LITERATURE CITED

[1] R. E. Kitson and M. G. Mellon, Ind. Eng. Chem. Anal. Ed., 16, 128 (1944).

[2] H. H. Krause and O. H. Johnson, Ind. Eng. Chem. Anal. Ed., 25, 137 (1953).

[3] A. S. Komarovsky and N. S. Poluetkov, Mikrochemie, 18, 66 (1935).

[4] D. F. Boltz and M. G. Mellon, Anal. Chem., 19, 873 (1947).

[5] W. Gelimann and K. Brunger, Biochem. Z., 275, 375 (1935).

[6] N. S. Poluektov, Z. anal. Chem., 105, 23 (1936).

[7] P. Cazeneuve, Comptes rend., 131, 346 (1900).

[8] F. Feigl, Qualitative Analysis by Spot Tests. Elsevier Press, Inc., New York, p. 48 (1947).

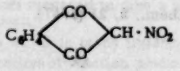
BLANK
PAGE

A SPECIFIC REACTION FOR FORMALDEHYDE

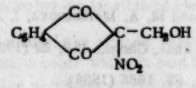
G. Vanag and E. Vanag

The Institute of Chemistry, Acad. Sci. Latvian SSR, Riga.

Nitro compounds which contain a hydrogen atom alongside the nitro group condense readily with formaldehyde. Thus, Gorsky and Makarov [1], showed that nitromethane can condense with 1, 2, or 3 molecules of formaldehyde, according to the experimental conditions; many similar examples are known. It was to be expected, therefore, that 2-nitroindanedione-1,3 (I), which contains a very mobile hydrogen next to the nitro group, would condense with formaldehyde. This in effect, does happen, for when concentrated formalin is placed on crystals of nitroindanedione, the same crystals, without going into solution, are converted into a thick, yellow oil, which is readily soluble in ether [2]. Nitroindanedione itself is insoluble in ether.



(I)



(II)

If a dilute formaldehyde solution is added to an aqueous solution of nitroindanedione, there is only partial formation of this same yellow oil, the main product being a white solid which is insoluble in ether; these two reaction products can accordingly be readily separated from each other. If normal condensation occurs between nitroindanedione and formaldehyde, one would expect the formation of 2-nitro-2-hydroxymethylindanedione-1,3 or β-phthalyl-β-nitroethanol (II). In actual fact, the composition of both reaction products corresponds to the latter formula; the reaction products actually obtained do not exhibit the properties one would expect for this compound, i.e., (II). The yellow oil is a rather unstable compound which easily decomposes into its component parts. It is possible that it may be an acetal or an acylal or even a molecular compound of the two components, similar to that which nitroindanedione gives with antipyrine, which is a molecular compound also in the form of a thick yellow oil [3].

The white solid is more stable and does not decompose into its components. It crystallizes poorly; it can, however, be obtained from ethyl acetate as crystals which melt at 145°. Neither the solid nor the yellow oil are monomers, but polymers (maybe trimers).

Both the thick yellow oil, and the white solid have one very interesting property in common, viz., when they are dissolved in concentrated sulfuric acid, and the resultant solution heated, an intense green fluorescence is obtained. This may be used as a characteristic reaction for formaldehyde.

Systematic investigation showed that other aldehydes do not condense with nitroindanedione; they cannot, therefore, give the fluorescence just mentioned. This reaction is accordingly specific for formaldehyde. Determination of formaldehyde may be carried out as follows. A little nitroindanedione (5-10 mg) is sprinkled into a test tube, 1-2 drops of the test solution added and the mixture stood for 15 minutes. 1 ml of concentrated sulfuric acid is then added and the whole carefully heated with a burner. After addition of sulfuric acid, the solution becomes yellow, but this color disappears rapidly; on heating, some gas is evolved (decomposition products of nitroindanedione), the liquid acquires a yellow or brown color, depending on the formaldehyde concentration, and the characteristic green fluorescence appears.

Using this technique, formaldehyde can be detected in two drops of 0.003% (0.001 M) solution, i.e., 3 γ of formaldehyde can be detected in 0.1 ml solution at a dilution of 1:33,000.

The following aldehydes do not give the characteristic fluorescence on testing in the same way: acetaldehyde, paraldehyde, chloralhydrate, acrolein, propionaldehyde, isobutyraldehyde, n-heptyraldehyde, crotonaldehyde, benzaldehyde, o-, m-, and p-nitrobenzaldehydes, salicylaldehyde, anisaldehyde, hydrocinnamaldehyde, furfural and heliotropine; the oxime of isovaleraldehyde, formamide, methanol, formic acid, and a number of other compounds closely related to formaldehyde do not give this characteristic fluorescence either. Only hexamethylenetetramine, which splits off formaldehyde, gives a positive reaction.

The reaction described is less sensitive than the Eegriwe [4], reaction with chromotropic acid, but it is simple and very specific.

The nitroindanedione is prepared by nitration of indanedione with an acetic acid solution of nitric acid, as described in published work [5, 6, 7].

SUMMARY

A new reaction, which is specific for formaldehyde, is described; crystals of 2-nitroindanedione-1,3 are wetted with test solution; after 15 minutes, concentrated sulfuric acid is added and the whole heated. If formaldehyde is present, a green fluorescence appears.

Received August 14, 1953

LITERATURE CITED

[1] I. M. Gorsky and S. P. Makarov, J. Gen. Chem., 4, 1006 (1934).

[2] G. Vanag, Bull. Acad. Sci. Latvian SSR, No. 8 (13), 56 (1948).

[3] G. Ya. Vanag and M. A. Matskanova, J. Anal. Chem., 2, 21 (1947).

[4] E. Eegriwe, Z. anal. Chem., 110, 22 (1937).

[5] G. Vanag, Ber., 69, 1066 (1936).

[6] B. Christensen, C. Wang, J. Davies, D. Harris, Anal. Chem., 21, 1573 (1949).

[7] L. Zalukaev and L. Sukhanova, Bull. Acad. Sci. Latvian SSR, 1952, No. 7 (60), 117.

CHARACTERISTIC CHROMATOGRAPHIC REACTIONS FOR GLUCOSE AND ACETONE

F. M. Shemyakin and O. S. Lobakhina

Moscow Pharmaceutical Institute

Colorimetric reactions for sugars, in particular for glucose have been studied many times. Colorimetric reactions for acetone have been studied to a considerably lesser extent.

The chemistry of the majority of these reactions, however, is far from being worked out thoroughly enough. This is the trouble with many colorimetric methods, as, for example, Kuznetsov and Babko [1], have pointed out. Most of these methods have found practical application before the mechanisms of the underlying reactions leading to to the formation of the respective colored compounds have been clarified. Fortunately, there are a few exceptions to this rule, e.g., the colorimetric determination of niobium by the method proposed by Alimarin and Podvalna [2]. In this particular instance the authors managed to give a very convincing explanation of the underlying mechanism, which had until then been unknown.

Chromatographic methods, which in many instances permit detection of some colored compounds, can give valuable results for the identification of reaction products. Thus, a color which is used for colorimetric purposes may, in some cases, be the sum total of separate colors belonging to several compounds and not to one compound.

A chromatographic variant of color reactions has the added advantage, that it permits one to get a "color spectrum" for a given reaction, which is more characteristic than the overall color. Chromatography also permits one to record the constancy of the composition, and the ratios of the colored compounds producing a given color, with the time that has elapsed from the start of a test, and with other experimental conditions. Babko [3], has paid particular attention to the variation of the composition of compounds used in colorimetry, with experimental conditions, and with time.

In the present article, we are suggesting chromatographic variants of some reactions for sugars (glucose) and for acetone with various reagents. In carrying out colorimetric reactions, some differently colored bands are obtained, which are spatially separated on paper surfaces or on adsorbent columns. In test tube reactions, only the sum total of all the individual colors is obtained. From this it follows that the chromatographic variant has one advantage, not hitherto made use of in analytical chemistry, and at the same time demonstrates the complexity of a color developed in a given reaction.

Reactions with Copper Citrate Reagent for Sugar (Glucose)

Reactions were carried out on three types of paper: chromatographic, prepared by Shemyakin's method [4], ordinary filter paper, and ashless filter paper. The developers used were: distilled water, and aqueous solutions of ethyl alcohol and acetone. Reactions were carried out with copper citrate reagent [5]. The following procedure was adopted: First of all, two drops of glucose solutions of various concentrations: 0.02, 0.1 and 2.4% were placed on the test paper. One drop of the copper citrate reagent was placed on the same spot on the filter paper, followed by 4-5 drops of the respective developer (water, alcohol, or acetone). The piece of filter paper with the spot on it was then heated at 100° for 3 minutes. A brightly colored chromatogram was thus obtained, which consisted of several concentric bands of varying colors and widths; this fact confirms that the overall color of the reaction product in this instance is made up of several individual colors. The color was examined both in daylight and under a quartz lamp. The largest bands were formed on the chromatographic and ashless filter papers. These experiments showed that, e.g., a spectrophotometric study of the colored solutions obtained when this reaction is used would be of use only after preliminary chromatographic separation of the colored products. Otherwise, a false absorption spectrum corresponding to the total color might be obtained, since it is known that any absorption spectrum may be imitated by a suitable mixture of colored compounds (synthetic colorimetric standards, e.g., made from inorganic salts).

Reactions with Copper Ions in Alkaline Media (by Trommer's Method)

In the course of this reaction hydrated copper oxide settles out unless something is present to dissolve it. Glucose dissolves hydrated copper oxide to form a blue colored compound in alkaline solution. The intensity of the color is proportional to the amount of glucose. On heating the blue liquid, yellow and red colors appear in the form of bands as the result of the formation of cuprous oxide, its hydrate, and of changes in the degree of dispersion.

The following solutions were prepared for this reaction: 1) a 10% solution of sodium hydroxide; 2) a 1% solution of cupric sulfate. The procedure adopted was as follows: 2 drops of glucose solution were first placed on a piece of filter paper, this was followed by one drop of sodium hydroxide, and finally one drop of the cupric sulfate solution. The piece of filter paper was then heated in an oven for 2-5 minutes at 100°. A yellow green spot developed on the chromatographic paper; the spot was surrounded by a light yellow band. On the periphery there was another band, which was colored brown with a red shade. Under a quartz lamp the chromatogram had the following appearance: a dark spot in the middle surrounded by a violet band and a red-brown band. On the periphery there was a very fine light blue band.

This chromatrographic technique, which we have developed for detection of sugar by means of two different reactions, has been successfully applied to the detection of glucose in urine.

We also prepared paper chromatograms of the urine of normal people and of diabetics, without addition of any reagents.

In all our tests, we used filter paper (ash 0.17%) and ashless filter paper —"blue ribbon" grade— ash 0.0002%, (Mendeleev Moscow Chem. Tech. Inst.), as well as chromatographic paper.

A definite number of drops of human urine is placed on the same spot on a piece of filter paper (10 X 10 cm). The primary chromatogram obtained can then be developed with distilled water, alcohol, or acetone. In individual experiments we put from 20 to 70 drops of urine on the paper. Paper thus soaked with urine in such amounts, did not acquire any bright and characteristic color, but was colored a pale yellow. Under a quartz lamp a series of brightly shining bands are observable on the paper. After developing with water, alcohol, or acetone, characteristic bands of various colors are obtained: violet, blue, dark blue, yellow. The greatest number of bands are obtained on chromatographic paper (up to seven concentric bands). Identification of the bands obtained by means of the various chemical compounds contained in them is a problem for further study. Such clear-cut and characteristic chromatograms as those obtained on paper are not obtained when columns of aluminum oxide of silica gel are used for urine analysis, as our experiments showed.

Reactions with Furfural for Acetone [6]

Reagents: 1) freshly prepared 1% solution of furfural in 95% alcohol; 2) concentrated hydrochloric acid; 3) 10% sodium hydroxide.

Acetone gives a red color with furfural. Two drops of acetone solution (containing one or a few grams of acetone per liter) were placed on filter paper, e.g., chromatographic paper, followed by one drop of furfural and one drop of sodium hydroxide solution in the center of the spot obtained. The piece of paper was heated at 100° and a drop of concentrated hydrochloric acid placed on the same spot. A bright red spot was formed, which did not change in intensity for 2-3 hours. The intensity depends on the amount of acetone. Under a quartz lamp up to eight bands were observable: bright yellow spot, dark-yellow, yellow, grey-yellow, black, grey-yellow, bright blue, grey-blue bands of differing widths, all concentric. All three types of paper gave similar chromatograms. Control tests in which no acetone was used gave no such bands. A bright red band was obtained on a silica gelcolumn. The following solutions were poured through the silica gel column: 2 ml of test solution, 2 ml of furfural solution, 2 ml sodium hydroxide, and 2 ml of hydrochloric acid —in that order. The advantage of carrying out this reaction on a column is that no heating is necessary. The band appeared without heating, at 1 cm from the upper edge of the adsorbent column; its width was 0.5 cm. Obviously, there is heating when the alkali reacts with acid.

Reactions with Sodium Nitroprusside for Acetone [7]

Reagents: 10% solution of sodium hydroxide; 10% sodium nitroprusside solution; glacial acetic acid (free from acetone).

Two drops of test acetone solution, one drop of nitroprusside solution, and one drop of alkali are placed on a piece of paper such as chromatographic paper. A red spot develops rapidly; a drop of acetic acid is then placed on the same place —the color of the spot changes to a cherry-red. At the center there is a yellow spot, while along the periphery there is a rose colored ring. Under a quartz lamp, the appearance of the chromatogram is as follows: a light grey spot in the center, surrounded by concentric cherry, grey, and light blue rings. Chromatographic paper gives the best results.

On silica gel columns, a cherry red band 0.5 cm wide is formed at a distance of 1-1.5 cm from the top of the column. The following solutions are passed successively through the column: 2 ml each of 1) acetone solution; 2) nitroprusside; 3) sodium hydroxide; 4) glacial acetic acid.

This method can be used for the detection of acetone in human urine.

The colors developed on paper and particularly on columns, last for days, for the reactions of acetone with both furfural and sodium nitroprusside, respectively.

Received February 19, 1954

LITERATURE CITED

[1] A. K. Babko and A. T. Pilipenko, "Colorimetric Analysis", State Chem. Press, 1951.

[2] I. P. Alimarin and R. D. Podvalnaya, J. Anal. Chem., 1, 30 (1946).

[3] A. K. Babko, J. Gen. Chem., 16, 968 (1946); 18, 816 (1948).

[4] F. M. Shemyakin, Symposium; "Research in Chromatography", Acad. Sci. USSR Press, 1952, p. 186.

[5] L. M. Kulberg, G. S. Alterzon, and R. P. Veltman, "Spot Analysis", State Chem. Press, 1951, p. 496.

[6] L. M. Kulberg, et. al., see [5], p. 492.

[7] V. S. Gulevich, "Urine Analysis", Medical Press, 1945, p. 55.

BLANK
PAGE

CRITICISM

R. Prshibil, "Complexones in Chemical Analysis", Czech. Acad. Sci. Press, Prague, 1953,* pp. 167, Price: 24 crowns (Kcs.)

The book, "Complexones in Chemical Analysis", by Prshibil, a State Prize Winner, is the first attempt in world literature to expound the work done in a new field of chemistry, viz., that of complexones, their theory, and practical application, in the form of a review.

Complexones, which are α-amino acids in which the nitrogen has not less than two (CH_2COOH)-groups attached to it, form such stable inner complex compounds with the majority of cations that it is impossible to prove the presence of the respective cation by ordinary analytical reactions. This enables complexones to be used on the one hand as masking agents, and on the other, as reagents in volumetric analysis. In addition, complexones enhance the sensitivity of several organic reagents.

Prshibil's monograph consists of two parts —a theoretical part, and the major part— a practical one, in which the application of complexones in chemical practice is discussed. The book contains 10 chapters and a large bibliography.

In the first part, which is made up of two chapters, viz., "The Theory of Complexones" and "Complex Forming Properties of Complexones", definitions and classifications are given, as well as methods for preparing known complexones. The following complexones are considered in this part: nitrilotriacetic acid, complexones containing one $-N(CH_2COOH)_2$-group, viz., derivatives of iminodiacetic acid, uramyl-N,N-diacetic acid, aniline-N,N-diacetic acid and its derivatives; these are followed by complexones containing two $-N(CH_2COOH)_2$ groups, viz., ethylenediaminetetracetic acid and its homologs, and finally, derivatives of diaminocyclohexane. In describing each complexone, the behavior of the complexone is considered under various conditions, as well as the conditions for the formation of complex compounds, their structure and character, and in conclusion the general characteristics of the respective groups of complexones are given. Tables of the values of the stability constants (Konstanta komplexity) for complexes formed between the majority of metal ions with given complexones are given for characterization of the stability of these complexes.

In the second and practical part of the book, the practical analytical application of complexones is discussed. In each chapter the principles underlying the reactions between complexones and test ions are set out, and examples given of the determination of metals on their own, and in the presence of others.

In the third chapter, "Complexones as Reagents for Volumetric Analysis", the author considers the determination of cations by titration of hydrogen ions liberated during formation of a complex, and direct titration with a standard solution of a complexone in the presence of specific indicators for some particular cation or other. The work of Schwarzenbach, Prshibil, Flashk and others is also considered in this chapter.

In Chapter IV, "Complexones as Reagents in Colorimetry", complexes of ethylenediaminetetracetic acid with the colored cations chromium, cobalt and manganese are described.

In Chapter V, "Complexone III (the Disodium Salt of Ethylenediaminetetracetic Acid) in Gravimetric Analysis", the author gives examples of how to carry out precipitation with the usual inorganic and organic reagents in the presence of Complexone III. For example, methods of determining beryllium, titanium, and uranium, either on their own or in the presence of each other, by precipitation with ammonia in the presence of Complexone III, are given. Considerable attention is given to the determination of molybdenum and tungsten in various ores in the presence of a number of other elements as contaminants by means of oxime.

In Chapter VI, "Complexones in Colorimetry", which is really a continuation of Chapter III, the enhanced selectivity of certain organic reagents in the presence of complexones is noted. Thus, dithizone, while being very sensitive, is not selective enough. Addition of a complexone increases the number of ions which can be determined by dithizone. A lot of attention is paid to the question of determining cobalt in the presence of iron, chromium, copper, and nickel, and also to the determination of traces of cobalt in nickel salts.

In Chapter VII, "Various Applications of Complexones", the use of complexones as masking agents is considered, as well as their use in potentiometric and amperometric titrations.

* R. Přibil, Komplexony v chemické analyse.

In Chapter VIII, "Complexones in Polarography", polarographic characteristics, and examples of practical application of Complexone IV (diaminocyclohexanetetracetic acid), which excels the other complexones in its properties, are considered. The practical application of volumetric reactions based on the different stability constants of the complex compounds of various metals with complexones is also considered in this chapter. It is possible to choose conditions such that the cation is quantitatively replaced in one of its complexes by another cation, the instability constant of which is less than the respective constant of the cation originally combined. This method is little known and could be widely used; zinc and cobalt can be determined in nickel, and nickel salts by this method.

In Chapter IX, "Complexones in Qualitative Analysis", the part played by complexones in the determination of ions by means of organic and inorganic reagents is discussed, finally Chapter X contains details of methods of analyzing complexones.

This monograph is of great value because it covers the various fields of application of complexones, so that the reader can bet a complete picture of the properties and value of this new class of compounds for the development of the most diverse fields of chemistry. The fact that Prshibil is the author of this book and at the same time has directed many researches in the field of complexones, and in setting forth the material in this book has used only work carried out by himself, considerably enhances the value of the monograph.

One of the drawbacks of the book is that it is rather condensed, and not enough is said about work carried out by Russian and other research workers.

So that as many analysts as possible should become acquainted with Prshibil's book, "Complexones in Chemical Analysis", it is very desirable that it should be translated into Russian.

November 12, 1954, Moscow

R. P. Lastovsky

CHRONICLE

The Conference on the Application of Complex Compounds in Analytical Chemistry held from October 25-27, 1954 at Ivanovo

A conference on the application of complex compounds in analytical chemistry, organized by the N. S. Kurnakov Institute of General and Inorganic Chemistry, Acad. Sci. USSR and the Ivanovo Institute of Chemical Technology, was held at Ivanovo from the 25-27th of October, 1954.

At the conference, 17 reports were read and discussed by scientific representatives of the Academy of Sciences USSR, the Ukrainian and Georgian Academies of Sciences, and of Moscow, Kiev, Kharkov, Kazan, Saratov and Voronezh Universities and of the Ivanovo Institute of Chemical Technology.

48 representatives were present at the conference. They came from Moscow, Leningrad, Kiev, Kharkov, Kazan, Saratov, Voronezh, Sverdlovsk, Odessa, Vilnyus, Kostroma, Alma-Ata, Tashkent, Chernovits, and other towns, as well as from the scientific-teaching collective of the Ivanovo Institute of Chemical Technology, and chemists from Ivonovo.

This conference is the first conference to have been devoted to the application of complex compounds in analytical chemistry.

Scientific workers occupied on research both in the field of complex compounds and in analytical chemistry attended the conference.

In a considerable number of the reports heard at the conference, questions relating to the theoretical bases of reactions of importance in analytical chemistry, to the investigation of equilibrium conditions, and to obtaining quantitative characteristics for complex compounds in aqueous solutions were considered.

The important part played by complex formation in various chemical-analytical methods was pointed out in the reports.

The conference also noted the fruitfulness of the application of N. S. Kurnakov's physico-chemical method to the investigation of complex formation and to the study of the thermodynamic characteristics of complex compounds. The results of these studies permit a correct evaluation of the use of a definite class of complex compounds in analytical chemistry to be made, to find optimal conditions for carrying out analytical reactions, and to establish the limits of applicability of existing methods of analysis.

Reports which dealt with analytical methods of determining individual elements were markedly fewer.

The number of reports on the investigation of complex formation in solution was also not enough. Thus, the very important method of marked atoms received hardly any attention.

There was very little work reported on the application of complex compounds in volumetric analysis and in electrochemical methods of analysis.

The Conference Regards It as Essential:

1) To continue research on physico-chemical analysis of solutions of complex compounds, by a study of the thermodynamics of complex formation in solution; to accumulate and systematize material on the instability constants of complex compounds which are important in analytical chemistry.

2) To expand the number of physico-chemical methods of studying complex formation in solution, and to use electrochemical, chromatographic, cryoscopic, and luminescence methods, as well as optical methods.

The conference in particular recommends that the method of marked atoms be used for studying the kinetics of complex formation, for determination of solubility, instability constants and other characteristics of complex compounds, and also to establish the accuracy of various chemical analytical methods.

3) The conference calls upon analytical chemists to pay more attention to studies directed toward a search for new analytical reactions and reagents for the determination of those elements for which only a few reactions are

known at present (tin, zinc, arsenic, antimony, and for anions). Particular attention should be given to the study of complex compounds and to the study of the analytical reactions of rare elements.

4) To continue research on the theoretical bases of reactions used in analytical chemistry (the study of equilibria in aqueous and non-aqueous solutions, extraction, sublimation of volatile compounds, etc.).

To study organic complex compounds, using the results of research for working out new methods of analyzing organic compounds. To pay attention to the study of reaction kinetics of complex formation. To study complex compounds in solution, it is essential that accurate quantitative characteristics (absorption spectra, molar extinction coefficients, etc.) should be used as much as possible.

5) With the aim of strengthening further the liaison between separate groups of research workers and increasing exchange of views, it is necessary to speed up the work of the "Commission for Coordinating Scientific Research Work" on the problems of "The Chemistry of Complex Compounds" at the N. S. Kurnakov Institute of General and Inorganic Chemistry. To strengthen the links between the branches of scientific research institutes and factory laboratories.

To call periodic conferences on individual topics, both on the chemistry of complex compounds and on analytical chemistry.

The conference would like to see the seventh All-Union Conference on the Chemistry of Complex Compounds held at Leningrad in 1956.

6) The conference deems it necessary to compile reviews and monographs on the chemistry of complex compounds, the physico-chemical analysis of complex compounds, the thermodynamics of complex formation, and also on individual methods of studying complex compounds. To request the State Chemical Press to issue hand books with tables of chemical constants (solubility products, instability constants, dissociation constants, oxidation-reduction potentials, etc.).

To ask the Foreign Literature Press to translate foreign monographs devoted to complex compounds and physico-chemical methods of analysis.

7) To ask the Commission on Analytical Chemistry of the USSR Academy of Sciences to put before the appropriate bodies requests to increase the supply of chemical reagents (including organic ones) and to issue new reagents (e.g., complexones, furyldioxime, cyclohexanedioxime, etc.) and extracting solvents (tributylphosphate, epichlorohydrin, methylbutyl ketone, etc.).

8) The conference wishes to turn attention to the necessity of increasing the supply of modern precision instruments for physico-chemical research on complex compounds (spectrophotometers, infra-red spectrophotometers, fluorimeters, electrical measuring instruments, ultra-centrifuges, etc.) and also to increase the supplies of spare parts for existing apparatus.

To bring up the question of constructing new types of apparatus for studying complex compounds. To consider it essential that all new models of apparatus issued should be tested by the Commission on Analytical Chemistry with the cooperation of leading scientific workers.

X-Ray Spectrographic Determination of Hafnium in Zirconium Minerals and Concentrates. p. 11.

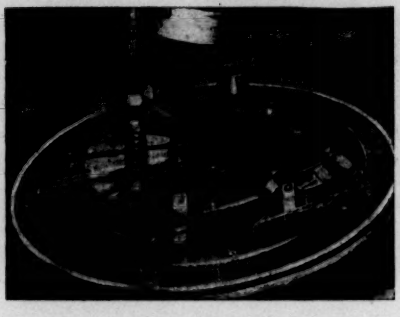


Fig. 1. General view of the vacuum X-ray spectrograph.

Fig. 4. The X-ray tube of the spectrograph.

Micro Determination of Carbon in Metals. p. 45.

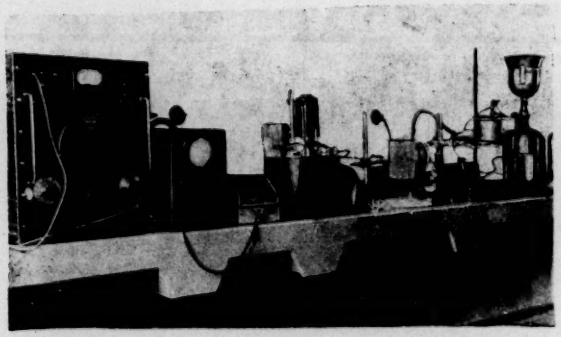


Fig. 7. General view of set-up.

BLANK
PAGE

BLANK
PAGE

TRANSLATIONS TO AND FROM ALL LANGUAGES

By bilingual chemists and engineers

Rates for translation into English:

Language	Price per 1000 words
French	$10.00
German	10.00
Italian	10.00
Russian	10.00
Spanish	10.00
Dutch	12.00
Other languages	Rates upon request

CONSULTANTS BUREAU
152 West 42nd Street
New York 18, N. Y.